

The Physical Basis of the Gibbs-von Neumann entropy.

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Abstract

We develop the argument that the Gibbs-von Neumann entropy is the appropriate statistical mechanical generalisation of the thermodynamic entropy, for macroscopic and microscopic systems, whether in thermal equilibrium or not, as a consequence of Hamiltonian dynamics. The mathematical treatment utilises well known results [Gib02, Tol38, Weh78, Par89], but most importantly, incorporates a variety of arguments on the phenomenological properties of thermal states [Szi25, TQ63, HK65, GB91] and of statistical distributions [HG76, PW78, Len78]. This enables the identification of the canonical distribution as the unique representation of thermal states without approximation or presupposing the existence of an entropy function. The Gibbs-von Neumann entropy is then derived, from arguments based solely on the addition of probabilities to Hamiltonian dynamics.

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1 Introduction

The laws of statistical mechanics apply to conservative systems of any number of degrees of freedom, and are exact.[Gib02]

The statistical mechanics considered by Gibbs, in his classic treatise of 1902, is a more general structure than thermodynamics. It applies to any kind of Hamiltonian system in which probabilistic reasoning is valid. Useful properties may be derived without any reference to thermodynamic quantities, and can be used without any consideration of whether or not one is dealing with a thermal system.

Nevertheless, thermal systems exist, are important and it is necessary that statistical mechanics gives an account of them, including the phenomena usually described by thermodynamics. Making this connection is surprisingly hard, without introducing “question begging” assumptions. Gibbs tentatively attempted to make this connection, in [Gib02][Chapter XIV], but only referred to thermodynamic “analogies”.

Criticisms of the Gibbs approach, and the Gibbs entropy as a *thermodynamic* entropy are not hard to find these days[Cal99, She99, Gol01, Alb01] and go back at least as far as[EE12]. The principal purpose of this paper, is to argue that the Gibbs-von Neumann entropy¹ can be derived, from physical arguments, without problematical assumptions, as precisely what one should desire for a *statistical* generalisation of *thermodynamic* entropy.

The method will not be to directly attempt to find statistical mechanical term to act as a thermodynamic entropy. There is no uncontroversial definition of entropy, outside of classical phenomenological equilibrium thermodynamics, but the world is not in equilibrium and statistical fluctuations occur. Instead the approach will be to develop statistical mechanics as a broader subject than thermal physics. When trying to apply statistical mechanics to thermal phenomena we will consider some basic physical properties of thermal states and then apply those properties to statistical mechanics.

Of central importance, and what differs most from more traditional treatments, will be the justification for the derivation of the canonically distributed density matrix as the unique statistical distribution that can represent thermal states. Here the key arguments will be Szilard’s 1925 derivation of the canonical distribution[Szi25] from phenomenological grounds, the concept of passive distributions[PW78, Len78, Sew80] and their relationship to the adiabatic availability of energy[HK65, HG76, GB91]. It is an interesting feature of these, that it does not depend upon whether the system is large or small or in thermal equilibrium or not. It applies to any situation in which the use of probability distributions are valid.

We will first explore the mathematical structure of Gibbs statistical mechanics, as applied to quantum mechanics. The mathematics will, in a large part be recognisable[Gib02, Tol38, Weh78, Par89], but the emphasis will be to show what can (and cannot) be derived *without* making physical assumptions. The section will, of necessity, appear rather abstract and unmotivated.

The structure so developed produces equations very like those that occur in thermodynamics. Actually connecting these equations with thermodynamics requires a logical jump which appears to assume precisely the thing which one seeks to justify. We will briefly review why this is so and some of the attempts to make this jump.

We then return to the physical basis of the statistical approach. The statistical approach applies whenever it is meaningful to use probabilities. Deciding when this is so is not uncontroversial, but we will not address that problem here. Instead we will explore what the consequences are when a probabilistic description is meaningful. A remarkably large amount of the familiar structure

¹We will be working with quantum mechanical systems, so will derive the von Neumann entropy.

of statistical mechanics can be derived without any reference to thermal concepts or notions of entropy. Particular attention will be drawn to the closely related concepts of adiabatic availability and passive distributions.

Only after we have derived the general structure of quantum statistical mechanics will we consider thermal systems. To examine what are the statistical mechanics of thermal systems, we first need to identify what we mean by a thermal system. We identify four physical properties, which we suggest are observed properties of thermal states. These properties uniquely select the canonical probability distribution. If this argument is accepted, we then proceed in well established steps to develop thermal heat baths, the temperature scale and finally the form of a statistical mechanical entropy from physically motivated arguments.

These physical arguments are valid for systems of any size, for non-equilibrium systems as well as for equilibrium systems, indeed for any situation where the use of a probability distribution is physically justified.

2 Mathematical formalism

We establish the properties of a particular type of function, which for want of a better word we shall call a distribution, on the state space of a system that has a Hamiltonian evolution. No physical interpretation is placed upon either this type of function nor of the derived properties. The object is to establish exactly which purely mathematical properties can be defined without needing to introduce physical justifications.

This section will, perhaps, seem needlessly abstract and physically unmotivated. This is quite correct! We develop the mathematics first to ensure that no physical assumptions have been used in their derivation. This is try to avoid circular reasoning when we come to consider the appropriate descriptions of physical processes.

When we do start to identify physical processes with mathematical structures, we wish to be clear which properties legitimate that identification, which properties then follow directly from that identification, and which properties require further assumptions or justification. Readers who are prepared to take this on trust may jump directly to Section 4 where we will start considering the properties of physical systems.

2.1 Distributions

The quantum mechanical state space is a Hilbert space Π and has a Hamiltonian evolution operator, $H(t)$. For the purposes of this paper, a distribution on the state space is an operator Ω on the state space, with orthonormal eigenstates $\{|\beta\rangle\}$ and real eigenvalues ω_β , for which:

$$\Omega = \sum_{\beta} \omega_{\beta} |\beta\rangle \langle\beta| \quad (1)$$

$$\omega_{\beta} \geq 0 \quad (2)$$

$$\sum_{\beta} \omega_{\beta} = 1 \quad (3)$$

$$i\hbar \frac{\partial \Omega}{\partial t} = [H, \Omega]_- \quad (4)$$

Both the eigenstates and eigenvalues may be evolving in time due to H . We may also write the time evolution of the distribution in the unitary form:

$$\Omega(t - t_0) = U\Omega(t_0)U^\dagger \quad (5)$$

where U is the solution of the operator equation

$$i\hbar \frac{\partial U}{\partial t} = HU \quad (6)$$

or in the more general superoperator form:

$$\Omega(t - t_0) = L(t - t_0) [\Omega(t_0)] \quad (7)$$

We will refer to the combination of a state space Π , Hamiltonian evolution H on the state space, and distribution Ω over the state space as a system.

2.1.1 Subdistributions

A subdistribution is the normalised portion of a distribution that is non-zero over a restricted region $R \subset \Pi$ of the state space:

$$\Omega_i = \sum_{\beta \in R} \frac{\omega_\beta}{\sum_{\beta \in R} \omega_\beta} |\beta\rangle \langle \beta| \quad (8)$$

Two subdistributions are non-overlapping if there is no region of the state space for which they are both non-zero:

$$\Omega_i \Omega_j = \delta_{ij} (\Omega_i)^2 \quad (9)$$

A distribution may be decomposed into non-overlapping subdistributions:

$$\Omega = \sum_i w_i \Omega_i \quad (10)$$

It will be useful to do this by constructing a complete set of non-overlapping projectors, K_i , such that

$$K_i K_j = \delta_{ij} K_i \quad (11)$$

$$\sum_i K_i = I \quad (12)$$

constructed from the eigenstates of the distribution:

$$\Omega = \sum_\alpha \omega_\alpha |\alpha\rangle \langle \alpha| \quad (13)$$

$$\langle \alpha | \alpha' \rangle = \delta_{\alpha\alpha'} \quad (14)$$

$$K_i = \sum_{\alpha \in i} |\alpha\rangle \langle \alpha| \quad (15)$$

$$\Omega_i = \frac{K_i \Omega K_i}{\text{Tr} [K_i \Omega K_i]} \quad (16)$$

$$w_i = \text{Tr} [K_i \Omega K_i] \quad (17)$$

2.1.2 Subspaces

When the Hilbert space can be separated into a product of two subspaces $\Pi = \Pi_1 \otimes \Pi_2$ we form the marginal distributions

$$\overline{\Omega}_1 = \text{Tr}_2 [\Omega] \quad (18)$$

$$\overline{\Omega}_2 = \text{Tr}_1 [\Omega] \quad (19)$$

The marginal distributions do not generally evolve by a Hamiltonian evolution, but the evolution may still be expressed by a superoperator equation:

$$\overline{\Omega}_1(t) = L_1 [\overline{\Omega}_1(0)] \quad (20)$$

2.2 Operators

Given an operator $A(t)$, on the state space, we may define the value of that operator for the distribution $\Omega(t)$ by:

$$\langle A(t) \rangle_{\Omega(t)} = \text{Tr} [A(t)\Omega(t)] \quad (21)$$

Given the Hamiltonian evolution operator $H(t)$, for the state space, then

$$i\hbar \frac{\partial \langle A(t) \rangle_{\Omega(t)}}{\partial t} = i\hbar \left\langle \frac{\partial A(t)}{\partial t} \right\rangle_{\Omega(t)} + \langle [A(t), H(t)]_- \rangle_{\Omega(t)} \quad (22)$$

If the system is not isolated, then it is a subsystem Π_1 of a larger space $\Pi = \Pi_1 \otimes \Pi_2$. The Hamiltonian may be rewritten as the sum of three terms:

1. A term operating solely upon subsystem 1, $H_1(t)$;
2. A term operating solely upon subsystem 2, $H_2(t)$;
3. and a term operating jointly as an interaction between the two systems $V_{12}(t)$.

$$H(t) = H_1(t) \otimes I_2 + I_1 \otimes H_2(t) + V_{12}(t) \quad (23)$$

Now the evolution of the marginal distribution $\overline{\Omega_1(t)} = \text{Tr}_2 [\Omega(t)]$ will not, in general, be describable by a Hamilton evolution operator.

If we take an operator $A_1(t)$ that acts solely upon the space of the subsystem Π_1 , we find:

$$i\hbar \frac{\partial \langle A_1(t) \otimes I_2 \rangle_{\Omega(t)}}{\partial t} = i\hbar \left\langle \frac{\partial A_1(t)}{\partial t} \right\rangle_{\overline{\Omega_1(t)}} + \langle [A_1(t), H_1(t)]_- \rangle_{\overline{\Omega_1(t)}} + \langle [A_1(t) \otimes I_2, V_{12}(t)]_- \rangle_{\Omega(t)} \quad (24)$$

Unless $[A_1(t) \otimes I_2, V_{12}(t)]_- = 0$ we appear to have a dependency upon the full distribution $\Omega(t)$. To eliminate this we express the evolution of the marginal distribution through the evolution of its eigenstates and eigenvalues:

$$\overline{\Omega_1(t)} = \sum_{\alpha} \omega_{\alpha}(t) |\alpha(t)\rangle \langle \alpha(t)| \quad (25)$$

The set of eigenstates $\{|\alpha(t)\rangle\}$ will always be a basis for the subspace, so there exists an unitary operator $\Upsilon(t)$ for which

$$|\alpha(t)\rangle = \Upsilon(t) |\alpha(0)\rangle$$

and whose evolution is generated by a Hamiltonian operator $\Theta(t)$:

$$i\hbar \frac{\partial \Upsilon(t)}{\partial t} = \Theta(t) \Upsilon(t)$$

This gives

$$i\hbar \frac{\partial \langle A_1(t) \rangle_{\overline{\Omega_1(t)}}}{\partial t} = i\hbar \left\langle \frac{\partial A_1(t)}{\partial t} \right\rangle_{\overline{\Omega_1(t)}} + \sum_{\alpha} i\hbar \langle \alpha(t) | A_1(t) | \alpha(t) \rangle \frac{\partial \omega_{\alpha}(t)}{\partial t} + \langle [A_1(t), \Theta(t)]_- \rangle_{\overline{\Omega_1(t)}} \quad (26)$$

which is expressed purely in terms of operators upon, and a distribution over, the subspace.

Note that if any of the commutators $[A_1(t), \Theta(t)]_-$, $[\overline{\Omega_1(t)}, A_1(t)]_-$ or $[\Theta(t), \overline{\Omega_1(t)}]_-$ are zero, the third term disappears to give:

$$\frac{\partial \langle A_1(t) \rangle_{\overline{\Omega_1(t)}}}{\partial t} = \left\langle \frac{\partial A_1(t)}{\partial t} \right\rangle_{\overline{\Omega_1(t)}} + \sum_{\alpha} \langle \alpha(t) | A_1(t) | \alpha(t) \rangle \frac{\partial \omega_{\alpha}(t)}{\partial t} \quad (27)$$

The following two terms will be useful later on:

$$\Delta A_1(t) = \int_0^t \frac{\partial \langle A_1(t) \rangle_{\overline{\Omega_1(t)}}}{\partial t} dt = \langle A_1(t) \rangle_{\overline{\Omega_1(t)}} - \langle A_1(0) \rangle_{\overline{\Omega_1(0)}} \quad (28)$$

$$D[A_1(t)] = \int_0^t \left\langle \frac{\partial A_1(t)}{\partial t} \right\rangle_{\overline{\Omega_1(t)}} dt \quad (29)$$

2.3 Gibbs-von Neumann measure

We now introduce the Gibbs-von Neumann measure of a distribution:

$$G[\Omega] = \text{Tr} [\Omega \ln [\Omega]] \quad (30)$$

There may be the perception that we have introduced a “question begging” step, as to why we introduce this particular measure. We suggest that this is not the case, as we have made no physical interpretation of this measure. We introduce it simply to establish some of its mathematical properties, devoid of any interpretation.

2.3.1 Concavity

The Gibbs-von Neumann measure is a concave function and this has the property, that given any two distributions Ω and Ω' , then

$$\text{Tr} [\Omega (\ln [\Omega] - \ln [\Omega'])] \geq 0 \quad (31)$$

2.3.2 Subspaces

When a space can be separated into two subspaces $\Pi = \Pi_1 \otimes \Pi_2$, we can define a measure of the correlation of the distribution between the subspaces as:

$$C[\Omega] = G[\overline{\Omega_1}] + G[\overline{\Omega_2}] - G[\Omega] \geq 0 \quad (32)$$

Equality occurs if, and only if, the systems are uncorrelated $\Omega = \overline{\Omega_1} \otimes \overline{\Omega_2}$.

This has a direct consequence for the evolutions of initially uncorrelated systems that are allowed to interact. If the systems are uncorrelated at $t = 0$, so that $\Omega(0) = \Omega_1(0) \otimes \Omega_2(0)$ but allowed to interact after that point, then for all $t > 0$

$$G[\overline{\Omega_1(0)}] + G[\overline{\Omega_2(0)}] \geq G[\overline{\Omega_1(t)}] + G[\overline{\Omega_2(t)}] \quad (33)$$

with equality occurring at time t if, and only if, $\Omega(t) = \overline{\Omega_1(t)} \otimes \overline{\Omega_2(t)}$

2.4 Canonical distribution

The extremal of $G[\Omega]$ for a fixed value of $\langle H \rangle_\Omega = E$ is given by the canonical distribution:

$$\Omega^{(\beta)} = \frac{e^{-\beta(E)H}}{\text{Tr} [e^{-\beta(E)H}]} \quad (34)$$

where $\beta(E)$ is a parameter depending only on the Hamiltonian H and the fixed value E .

We will assume that the extremal value is always the minimal value, although this is a far from trivial assumption.

2.4.1 Subspaces

If there is no interaction term between subspaces of a canonically distributed system, the marginal distributions over the subspaces are canonically distributed with the same β parameter.

$$H = H_1 \otimes I_2 + I_1 \otimes H_2 \quad (35)$$

$$\Omega^{(\beta)} = \frac{e^{-\beta H_1}}{\text{Tr}[e^{-\beta H_1}]} \otimes \frac{e^{-\beta H_2}}{\text{Tr}[e^{-\beta H_2}]} \quad (36)$$

2.4.2 Minimising $G + \beta \langle H \rangle$

Given a state space, a Hamiltonian H , the canonical distribution $\Omega^{(\beta)}$ for that Hamiltonian and any other distribution Ω' over that space, then:

$$G[\Omega'] + \beta \langle H \rangle_{\Omega'} \geq G[\Omega^{(\beta)}] + \beta \langle H \rangle_{\Omega^{(\beta)}} \quad (37)$$

The canonical distribution not only minimises G for a fixed value of $\langle H \rangle$ but also minimises $G + \beta \langle H \rangle$ for a fixed value of β .

The result can be rearranged to give

$$G[\Omega'] - G[\Omega^{(\beta)}] \geq -\beta (\langle H \rangle_{\Omega'} - \langle H \rangle_{\Omega^{(\beta)}}) \quad (38)$$

2.4.3 Interactions with arbitrary distributions

Interactions between a canonically distributed system $\Omega_1^{(\beta)}$ and an arbitrarily distributed system Ω_2 .

They are initially ($t = 0$) non-interacting $H = H_1 \otimes I_2 + I_1 \otimes H_2$ and uncorrelated $\Omega(0) = \Omega_1^{(\beta)}(0) \otimes \Omega_2(0)$. The systems are allowed to interact, $H' = H + V_{12}$, for a finite period of time, but so that at the end of the interaction $\langle H \rangle_{\Omega}(t) = \langle H \rangle_{\Omega}(0)$.

It can then be shown that

$$G[\overline{\Omega_2(0)}] + \beta \langle H_2 \rangle_{\overline{\Omega_2(0)}} \geq G[\overline{\Omega_2(t)}] + \beta \langle H_2 \rangle_{\overline{\Omega_2(t)}} \quad (39)$$

2.4.4 Interactions between canonical distributions

Interactions between two canonically distributed systems, but with different β parameters, $\Omega_1^{(\beta_1)}$ and $\Omega_2^{(\beta_2)}$.

They are initially ($t = 0$) non-interacting $H = H_1 \otimes I_2 + I_1 \otimes H_2$ and uncorrelated $\Omega(0) = \Omega_1^{(\beta_1)}(0) \otimes \Omega_2^{(\beta_2)}(0)$. The systems are allowed to interact, $H' = H + V_{12}$, for a finite period of time, outside which $\langle V_{12} \rangle_{\Omega(t)} = \langle V_{12} \rangle_{\Omega(0)} = 0$, but at the end of the interaction $\langle H \rangle_{\Omega(t)} = \langle H \rangle_{\Omega(0)}$.

It can be shown that

$$\beta_1 \left(\langle H_1 \rangle_{\overline{\Omega_1(t)}} - \langle H_1 \rangle_{\overline{\Omega_1(0)}} \right) + \beta_2 \left(\langle H_2 \rangle_{\overline{\Omega_2(t)}} - \langle H_2 \rangle_{\overline{\Omega_2(0)}} \right) \geq 0 \quad (40)$$

Using the notation:

$$\Delta H_1 = \langle H_1 \rangle_{\overline{\Omega_1(t)}} - \langle H_1 \rangle_{\overline{\Omega_1(0)}} \quad (41)$$

$$\Delta H_2 = \langle H_2 \rangle_{\overline{\Omega_2(t)}} - \langle H_2 \rangle_{\overline{\Omega_2(0)}} \quad (42)$$

$$\Delta H = \Delta H_1 + \Delta H_2 = 0 \quad (43)$$

this becomes

$$\Delta H_1 (\beta_1 - \beta_2) \geq 0 \quad (44)$$

2.5 Large uncorrelated canonical assemblies

We will now consider a particular type of system called a Large Uncorrelated Canonical Assembly.

- The system is large, in that it has a very large number of degrees of freedom.
- The distribution over the state space is uncorrelated with any other system.
- The distribution over the state space is a canonical distribution, with parameter β .
- The system is an assembly[Per93]. It consists of a very large number of identical subsystems, with no interactions between the subsystems.

As the overall distribution is canonical, and there are no interactions between subsystems, the subsystems have canonical distributions with the same parameter β and will not be correlated with each other.

2.5.1 Interactions with arbitrary distributions

When another system interacts with a LUCA system, the interaction will always be in a particular way. The interacting system will have a succession of brief interactions with successive subsystems of the LUCA, such that no subsystem of the LUCA is ever encountered twice.

As each interaction with a subsystem is an interaction with a canonical system with parameter β , by Equation 39 the value of $G[\overline{\Omega_2}] + \beta \langle H_2 \rangle_{\overline{\Omega_2(t)}}$ for the interacting system will increase on each interaction. If there is no further barrier to prevent it, this value will approach its maximum. From the results of Section 37, the distribution which maximises this is the canonical distribution over H_2 with the parameter β .

2.5.2 Interactions with canonical distributions

Now consider an interaction between a LUCA system and a system already canonically distributed with the same parameter β .

Consider a very slow variation in the Hamiltonian of the system from $H_1(0)$ to $H_1(t)$. We might suppose that we proceed in a series of small steps. First isolate the system and make a very small change in its Hamiltonian, sufficiently slowly that the quantum mechanical adiabatic theorem applies[Mes62][Ch 17]. As an isolated system the distribution will move slightly away from canonical. Then bring it back into contact with the LUCA, and the distribution will be restored to a canonical distribution with parameter β .

As the steps become infinitesimal, the system remains in the canonical distribution, but now it is a time varying canonical distribution:

$$\Omega_1^{(\beta)}(t) = \frac{e^{-\beta H_1(t)}}{\text{Tr}[e^{-\beta H_1(t)}]} \quad (45)$$

As this is always diagonalised in the $H_1(t)$ basis, we have

$$\frac{\partial \langle H_1(t) \rangle_{\overline{\Omega_1(t)}}}{\partial t} = \left\langle \frac{\partial H_1(t)}{\partial t} \right\rangle_{\overline{\Omega_1(t)}} + \sum_{\alpha} E_{\alpha}(t) \frac{\partial}{\partial t} \left(\frac{e^{-\beta E_{\alpha}(t)}}{\text{Tr}[e^{-\beta H_1(t)}]} \right) \quad (46)$$

where $E_{\alpha}(t)$ is the instantaneous energy eigenvalue of the instantaneous eigenstate $|E_{\alpha}(t)\rangle$ of $H_1(t)$.

Adding the identity

$$\frac{1}{\beta \text{Tr} [e^{-\beta H_1(t)}]} \frac{\partial}{\partial t} \text{Tr} [e^{-\beta H_1(t)}] + \frac{1}{\text{Tr} [e^{-\beta H_1(t)}]} \sum_{\alpha} e^{-\beta E_{\alpha}(t)} \frac{\partial E_{\alpha}(t)}{\partial t} = 0 \quad (47)$$

the last term can be rearranged

$$\begin{aligned} \sum_{\alpha} E_{\alpha}(t) \frac{\partial}{\partial t} \left(\frac{e^{-\beta E_{\alpha}(t)}}{\text{Tr} [e^{-\beta H_1(t)}]} \right) &= -\frac{\beta}{\text{Tr} [e^{-\beta H_1(t)}]} \sum_{\alpha} E_{\alpha}(t) e^{-\beta E_{\alpha}(t)} \frac{\partial E_{\alpha}(t)}{\partial t} \\ &\quad - \frac{1}{\text{Tr} [e^{-\beta H_1(t)}]^2} \sum_{\alpha} E_{\alpha}(t) e^{-\beta E_{\alpha}(t)} \frac{\partial}{\partial t} \text{Tr} [e^{-\beta H_1(t)}] \\ &\quad + \frac{1}{\beta \text{Tr} [e^{-\beta H_1(t)}]} \frac{\partial}{\partial t} \text{Tr} [e^{-\beta H_1(t)}] + \frac{1}{\text{Tr} [e^{-\beta H_1(t)}]} \sum_{\alpha} e^{-\beta E_{\alpha}(t)} \frac{\partial E_{\alpha}(t)}{\partial t} \\ &= \frac{\partial}{\partial t} \left(\frac{\sum_{\alpha} E_{\alpha}(t) e^{-\beta E_{\alpha}(t)}}{\text{Tr} [e^{-\beta H_1(t)}]} + \frac{1}{\beta} \ln [\text{Tr} [e^{-\beta H_1(t)}]] \right) \\ &= \frac{1}{\beta} \frac{\partial}{\partial t} \sum_{\alpha} \left(\frac{e^{-\beta E_{\alpha}(t)}}{\text{Tr} [e^{-\beta H_1(t)}]} \beta E_{\alpha}(t) + \frac{e^{-\beta E_{\alpha}(t)}}{\text{Tr} [e^{-\beta H_1(t)}]} \ln [\text{Tr} [e^{-\beta H_1(t)}]] \right) \\ &= -\frac{1}{\beta} \frac{\partial}{\partial t} \sum_{\alpha} \frac{e^{-\beta E_{\alpha}(t)}}{\text{Tr} [e^{-\beta H_1(t)}]} \ln \left[\frac{e^{-\beta E_{\alpha}(t)}}{\text{Tr} [e^{-\beta H_1(t)}]} \right] = -\frac{1}{\beta} \frac{\partial}{\partial t} G [\Omega_1^{(\beta)}(t)] \quad (48) \end{aligned}$$

Integrating Equation 46 from 0 to t then gives:

$$D [H_1(t)] = \Delta H_1(t) + \frac{1}{\beta} \Delta G [\Omega_1^{(\beta)}] \quad (49)$$

3 Not thermodynamics

The properties we have considered here are simply mathematical properties of the Hamiltonian evolution of distributions over state spaces. They will apply to any function that has the properties of being a distribution. No physical interpretation has been placed upon them, and no physical interpretation should be placed upon them unless it can be justified that the property concerned does, in fact, correspond to a physical property of interest.

We have introduced a particular measure, the Gibbs-von Neumann measure, which proves to have certain properties. We have also identified a particular distribution, which is uniquely selected by that measure. We have identified a particular type of system, which has that unique distribution. The resulting description produces equations that closely resemble thermodynamics. It is tempting to identify G with the negative of entropy and see Equation 33 as representing the Second Law of Thermodynamics. It is tempting to identify the canonical distribution as representing thermal equilibrium, as it is the state that maximises $-G$, to identify β as the reciprocal of temperature, on the basis of Equation 44, to identify an environmental heat baths as a LUCA on the basis of Section 2.5.1 and Equation 49 as the isothermal equation $\Delta W = \Delta E - T \Delta S$. But how justified is all this?

There are two problems. The first is why should one suppose $-G$ represents entropy or canonical distributions represent thermal equilibrium? The second is whether it is even valid to identify the thermodynamic entropy with a measure upon a distribution.

3.1 Why *these* distributions, these measures?

The first problem can be seen earliest in works such as [Gib02][Chapter XIV], where different distributions are discussed, which may also appear to reproduce thermodynamic results. Gibbs cautiously refers only to thermodynamic “analogies” in statistical mechanics (a practice echoed in [Tol38], amongst others).

In his review[Pen79], Penrose shows the question remains:

what is the physical significance of a Gibbs ensemble? How can we justify the standard ensembles used in equilibrium theory?

Let us consider the mathematical structure of the previous section. The properties derived are almost entirely consequences of two things:

1. The function G is a concave function of distributions (Section 2.3.1);
2. The sum of the marginal values of G for two uncorrelated distributions is greater than the sum of the marginal values of G for two correlated distributions (Section 2.3.2).

If we are tempted to identify G as entropy and β as temperature on the basis of the relationships derived, wouldn’t *any* non-decreasing, concave function, with the appropriate property for uncorrelated distributions², be able to do the job?

In recent years it has also been argued that, in quantum mechanics, it has simply been *assumed* that the von Neumann entropy is the appropriate one, and that the only justification offered for it is flawed:

The convention first appears in Von Neumann’s *Mathematical Foundations of Quantum Mechanics*. The argument given there to justify this convention is the only one hitherto offered. All the arguments in the field refer to it at one point or another. Here this argument is shown to be invalid.[She99]

If we assume that the canonical distribution is appropriate for thermal equilibrium, we may reasonably represent an ideal heat bath by a LUCA, and from this (for large thermal systems, at least) it is possible to show that the von Neumann entropy correctly gives the value of the thermodynamic entropy. But what is the justification for using the canonical distribution, except that it maximises the von Neumann entropy?

If we start by identifying a LUCA as an ideal heat bath, we can show that thermalisation corresponds to approaching the canonical distribution and so, perhaps, justify the canonical distribution as appropriate for thermalisation. But why assume that an ideal heat bath is a LUCA? A LUCA is canonically distributed already, so assuming that it represents an environment at some temperature is tantamount to assuming the very thing we would wish to demonstrate.

If we assume that the von Neumann entropy is the thermodynamic entropy, then maximising it produces the canonical distribution. This may justify the canonical distribution as thermal equilibrium and hence LUCA’s as ideal heat baths. But, without assuming the canonical distribution is thermal equilibrium in the first place, what reason do we have for believing the von Neumann entropy is thermodynamic entropy?

Although we appear to have arrived at expressions that are analogous to thermodynamic expressions, we cannot identify these expressions with thermodynamic processes unless we can be sure that they really are the appropriate representation of the physical process. There appears to be a logical gap.

²Technically this property can be obtained for G from (a) concavity; and (b) the value of G being additive for uncorrelated distributions. It is only G that has this property. However, this additivity is *not* necessary for the derived property to hold, so the derived properties may still hold for other, non-additive, concave functions.

3.1.1 Why the canonical distribution?

There has been a large literature devoted to deriving the canonical distribution. Attempts in the literature to justify the canonical distribution are largely to do with the problem of explaining the approach to thermal equilibrium. It is assumed that the canonical distribution is thermal equilibrium (and an entropy usually has already been decided upon), and the attempt is to explain why systems are *in* thermal equilibrium. While this is not the same as our concern here, it will be useful to briefly review these attempts.

The Ehrenfests[EE12][Section 25] credit Boltzmann with the first observation which justifies the canonical ensemble. The essence of this justification is that if one takes a large system, whose distribution is uniform over a constant energy hypersurface (i.e. a microcanonical distribution), and one takes a small subsystem of that, then the marginal distribution of the small subsystem is canonical. Indeed, with minor variations, this relationship between the microcanonical and canonical distributions, is practically the *only* justification offered in most textbooks.

The problem then becomes to justify the microcanonical distribution. Some, following Tolman, simply make a fundamental assumption of a uniform distribution, with the only justification being, in effect, the Principle of Insufficient Reason to argue the inappropriateness any other choice.

Attempts to justify the uniform distribution on dynamical grounds, argued by the Ehrenfests, have led to the development of the Boltzmann’s ergodic hypothesis, concepts such as metric transitivity, and weak and strong mixing. Although this has generated much interesting mathematics, as a justification of the microcanonical distribution for realistic systems, it can only be said to have had a mixed degree of success (see [BFK06] for a discussion and defense).

A recent development[PSW06, GLTZ06] of Boltzmann’s original insight, specific to quantum mechanics, demonstrates that for large systems in a *pure* quantum state, the reduced density matrix of a small subsystem is very close to being canonically distributed. This appears to produce the canonical distribution even without needing a probability distribution over the whole space. Unfortunately the result is not true for all pure states, only “almost every” or the “overwhelming majority” of such states. The problem here is that these terms are only valid relative to some measure over the state space and, as it turns out, that measure is the uniform one. In other words, the development shows that it is overwhelmingly *probable* that the individual subsystem behaves as if it is canonically distributed, *if* we have a uniform probability distribution over the whole state space. While this is a stronger result than Boltzmann’s, it cannot be said to have less problematical assumptions.

3.1.2 Why the Gibbs-von Neumann measure?

Once the Gibbs-von Neumann entropy is chosen as physical entropy, it is possible to argue that the canonical distribution is appropriate for thermal equilibrium as it maximises the entropy of thermally isolated systems.

Our problem here is why the Gibbs-von Neumann entropy should be used at all. This measure can certainly be uniquely identified from a number of information theoretic prescriptions[Sha48, SW49]. But why should such information theoretic concerns should be of any significance for thermodynamics? Why should *thermal* equilibrium have anything to do with maximising our lack of knowledge?

The idea that entropy is something to do with a lack of knowledge or uncertainty is an old one, but unless one has already assumed that the measure of entropy is indeed a function of probability what is the basis for believing that thermodynamic entropy *should* have anything to do with uncertainty? A priori, what *is* the property of thermal states that make us think they represent

maximal ignorance? Even if this is accepted, there are many measures of ignorance. Why are the properties of the Shannon measure of information the ones that identify the function that needs maximising? The existence of alternate information measures, such as the Renyi measures, and alternate entropy measures, such as the Tsallis entropy[Tsa88, Tsa00, Tsa03] and others[CB07, Cam07] call into question whether assumptions that uniquely specify the Shannon measure can be taken for granted.

3.2 Why distributions? What is entropy anyway?

The second problem is the complaint of authors such as:

The Gibbs entropy is not even an entity of the right sort: It is a function of a probability distribution, i.e., of an ensemble of systems, and not a function on phase space, a function of the actual state X of an individual system[Gol01]

thermodynamic entropy is patently an attribute of *individual systems*. And attributes of individual systems can patently be nothing other than attributes of the *individual microconditions*.[Alb01]

for present purposes - reconciling thermodynamics with mechanics - [Gibbs entropy] is of no use since thermodynamic entropy is applicable to individual systems. My coffee in the thermos has an objective thermodynamic entropy as a property.[Cal04]

The literature abounds with alternative definitions of entropy (in a recent work[CS05][Chapter 1] 21 different versions of entropy are listed). Perhaps the question should not be “What is the correct expression for entropy?”, but “What exactly is ‘entropy’ supposed to *be*?”. What is it about a particular expression that legitimates referring to it as ‘entropy’? What, in short, is ‘entropy’ *for*? To develop a physical understanding of this, we will let the answer emerge *from* statistical mechanics, rather than be presupposed.

4 Statistical Mechanics

After having asked many questions in the previous Section, we will now proceed by ignoring them. We will develop statistical mechanics without any reference to entropy at all. The main purpose of this is to demonstrate that much of the physical understanding of statistical mechanics may be developed without any reference to thermodynamics.

The basic assumption of this section is that we have a physical system of interest where it is valid to talk about a probability of the system being in a particular state. We will not consider why such a probabilistic situation has occurred, and will attempt to avoid all discussion of what ‘probability’ actually means. Instead we will take for granted that we are dealing with situations where statements of the form “There is a probability $p(X)$ that the system is in state X ” are meaningful, and work through the consequences of this. From now on, when we refer to a system, we will mean a physical system, with a state space, a Hamiltonian evolution and probability for the system being in any particular state.

4.1 Operators and evolutions

To go back to basics, we start by deciding what we can say about the average value of observing an observable. Suppose we have an observable A , then the expectation value of the observable, when

the system is in state $|\alpha_n\rangle$ is $\langle\alpha_n|A|\alpha_n\rangle$. If the state $|\alpha_n\rangle$ has probability $p(\alpha_n)$, then expectation value of the observable is

$$\langle A \rangle = \sum_n p(\alpha_n) \langle\alpha_n|A|\alpha_n\rangle \quad (50)$$

This can be rewritten as

$$\langle A \rangle = \text{Tr}[\rho A] \quad (51)$$

where

$$\rho = \sum_n p(\alpha_n) |\alpha_n\rangle \langle\alpha_n| \quad (52)$$

(Note we have not assumed that the set $\{|\alpha_n\rangle\}$ are an orthonormal basis).

ρ is the density matrix for the system. All the statistical properties of the system can be calculated from the density matrix. As well as mean values we may also calculate variances, standard deviations, and indeed all of the standard apparatus of statistics and probability theory.

We also note that the density matrix fulfils the criteria for a distribution, provided that (for isolated systems, at least), if the state $|\alpha_n\rangle$ at time $t = 0$, has probability $p(\alpha_n)$, the state evolves into $|\alpha'_n\rangle$ at a later time $t = \tau$, by a Hamiltonian evolution and state $|\alpha'_n\rangle$ has probability $p(\alpha_n)$.

At the risk of further stating the obvious, let us just remember a few other things. The expectation value is not telling us the exact value that we will actually get, nor is it even telling us that the value we will actually get is close to this value. We should no more expect this than expect that when we roll a die, the face should come up with a number close to three and a half.

The value we get is an expectation value, because that is the statistical property we have chosen to calculate. Statistics is certainly not limited to calculating expectation values! If we want to calculate other statistical properties, perform other statistical operations, the density matrix certainly allows us to do so. If we find physical reasons for preferring other statistics, then those other statistics are what we should use. There is nothing intrinsically special to expectation values! Finally, to avoid cumbersome words, from now on we will refer to the expectation value of properties as the mean value.

4.2 Isolated systems

If, as is usual, we identify the Hamiltonian as the energy operator, then the mean energy of the system is

$$\langle H \rangle_\rho = \text{Tr}[H\rho] \quad (53)$$

We now consider how this mean value varies with time.

4.2.1 Work

For an isolated³ system, the density matrix evolves unitarily:

$$i\hbar \frac{\partial \rho}{\partial t} = [H, \rho]_- \quad (54)$$

so the mean energy changes:

$$\frac{\partial \langle H \rangle_\rho}{\partial t} = \left\langle \frac{\partial H}{\partial t} \right\rangle_\rho \quad (55)$$

³Note that we do not take isolated to mean having a time independant Hamiltonian. We take isolated to mean only that there is no interaction Hamiltonian with another system.

Still back to basics, we might ask what this means. The left hand side is clearly the rate at which the mean energy of the system is changing. What of the right?

Let us suppose that the Hamiltonian is a function of some parameters (x, y, z) that are varying in time:

$$H = \sum_n E_n(x, y, z) |E_n(x, y, z)\rangle \langle E_n(x, y, z)| \quad (56)$$

The eigenstates can be rewritten

$$|E_n(x, y, z)\rangle = \Upsilon(x, y, z) |E_n\rangle \quad (57)$$

so that the operator

$$\frac{\partial H}{\partial t} = \sum_n \dot{\underline{x}} \cdot \nabla E_n(x, y, z) |E_n(x, y, z)\rangle \langle E_n(x, y, z)| + [\dot{\underline{x}} \cdot \underline{\Theta}, H]_- \quad (58)$$

where

$$\dot{\underline{x}} = \left(\frac{\partial x}{\partial t}, \frac{\partial y}{\partial t}, \frac{\partial z}{\partial t} \right) \quad (59)$$

$$\underline{\Theta} = \left(\frac{\partial \Upsilon(x, y, z)}{\partial x} \Upsilon^\dagger(x, y, z), \frac{\partial \Upsilon(x, y, z)}{\partial y} \Upsilon^\dagger(x, y, z), \frac{\partial \Upsilon(x, y, z)}{\partial z} \Upsilon^\dagger(x, y, z) \right) \quad (60)$$

The first part of Equation 58 should be recognised as the generalised force $\nabla E_n(x, y, z)$ that comes from the change in energy eigenvalues due to a change in the parameters (x, y, z) . The product with the rate of change of those parameters gives the rate of work against the force.

The second part is slightly more subtle. If the energy eigenstates are varying, then, if we were to keep the energy eigenvalues and the state of the system fixed, the expectation value of the energy for that state would be changing. This term, therefore, represents the rate of work required to rotate the energy eigenstates.

The term $\langle \alpha_n | \frac{\partial H}{\partial t} | \alpha_n \rangle$ gives the mean rate of work required for state $|\alpha_n\rangle$, so $\left\langle \frac{\partial H}{\partial t} \right\rangle_\rho$ is just the mean rate of work required, given the density matrix ρ .

So, the rate at which the mean energy of the system is changing is equal to the mean rate at which work is being performed upon the system. Given the systems is isolated, we should hope so!

4.2.2 Adiabatic availability

We now ask the question: how much work may be extracted from a given state ρ , by a cyclic variation of the system Hamiltonian⁴ H ? We will call this the adiabatic availability of the state ρ (see [GB91][Chapter 5]). We assume that the system is completely isolated. Clearly the work extracted by a variation in the Hamiltonian is given by

$$W = - \int_0^\tau \frac{\partial \langle H \rangle_\rho}{\partial t} dt \quad (61)$$

As the system is isolated, the evolution of ρ depends solely upon H , and we require that $H = H_0$ for all $t < 0$ and $t > \tau$. This allows us to rewrite the result, rather trivially, as:

$$W = -\text{Tr} \left[H_0 U^\dagger(\tau) \rho_0 U(\tau) - H_0 \rho_0 \right] \quad (62)$$

⁴Note, here, that this is a cyclic variation in the Hamiltonian, *not* the state of the system. This is not, therefore, directly related to the Kelvin statement of the second law.

where

$$\rho_0 = \sum_n \lambda_n |n\rangle \langle n| \quad (63)$$

is the initial density matrix,

$$i\hbar \frac{\partial U(t)}{\partial t} = H(t)U(t) \quad (64)$$

and $U(0) = I$.

We would clearly like to extract as much work as possible from the system. Is there a limit to how much we can extract? If the initial Hamiltonian H_0 is not bounded from below (i.e. does not have a ground state with finite energy) then the answer is, no, there is no limit. Excluding this case, the answer is, yes.

4.2.3 Passive distributions

Let us note that Equation 62 expresses the difference between the mean energy of the initial density matrix ρ_0 , and another density matrix which can be related to it by a unitary transformation $U(\tau)$. To get the most work out, it is therefore necessary to vary the Hamiltonian so as to minimise the mean energy of the state $\rho(\tau) = U^\dagger(\tau)\rho_0 U(\tau)$. As $\rho(\tau)$ must have the same eigenvalues as ρ_0 , it turns out that the minimum is just the state which is diagonalised in the energy eigenstates

$$\rho(\tau) = \sum_n p_n |E_n\rangle \langle E_n| \quad (65)$$

such that

$$p_m \geq p_n \Leftrightarrow E_m \leq E_n \quad (66)$$

A density matrix which satisfies these criteria is called a passive distribution. Intuitively it is clear that a passive distribution must certainly minimise the internal energy for a set of eigenvalues, if diagonalised in the energy eigenstates. If Equation 66 did not hold, for two given states, it would always be possible to reduce the mean energy (and extract work) by swapping those two states.

We now show that density matrices that are not diagonalised by the energy eigenstates are not passive. Take a density matrix which is assumed to not be diagonalised in the energy basis:

$$\rho_1 = \sum_j \lambda_j |\Lambda_j\rangle \langle \Lambda_j| \quad (67)$$

with the ordering $\lambda_i \geq \lambda_j \Leftrightarrow i \leq j$, and form the density matrix diagonalised in the energy basis:

$$\rho_2 = \sum_i \mu_i |E_i\rangle \langle E_i| = \sum_i \langle E_i | \rho_1 | E_i \rangle |E_i\rangle \langle E_i| \quad (68)$$

for which clearly $\text{Tr}[H\rho_1] = \text{Tr}[H\rho_2]$. Now compare ρ_2 with the passive distribution

$$\rho_3 = \sum_j \lambda_j |E_j\rangle \langle E_j| \quad (69)$$

As the eigenvalues are related by a doubly stochastic map

$$\mu_i = \sum_j |\langle E_i | \Lambda_j \rangle|^2 \lambda_j \quad (70)$$

it follows[HLP34] that

$$\sum_i \mu_i E_i \geq \sum_j \lambda_j E_j \quad (71)$$

with equality possible if and only if the doubly stochastic map is a permutation. For the μ_i distribution to be passive, this would require an identity map, which is not the case by assumption. It follows that $\text{Tr}[H\rho_1] > \text{Tr}[H\rho_3]$, but ρ_3 is clearly accessible from ρ_1 by a unitary map. ρ_1 is therefore not passive.

For any given density matrix ρ and Hamiltonian H_0 , there is a passive distribution $\tilde{\rho}$ with the same eigenvalues. The adiabatic availability is then:

$$A[\rho, H_0] = \text{Tr}[H_0(\rho - \tilde{\rho})] \geq 0 \quad (72)$$

Equality is reached only for passive distributions, which all have adiabatic availabilities of zero. The adiabatic availability is always uniquely defined although the passive distribution is unique only if the energy eigenvalues are non-degenerate.

For an isolated system it is clearly the case that the work performed upon the system, in any cyclic variation of the Hamiltonian, must equal the change in adiabatic availability. For a non-cyclic variation in the Hamiltonian, this is not the case. If $H_0 \rightarrow H_1$ leads to $\rho_0 \rightarrow \rho_1$ then the work W and change in adiabatic availability ΔA are related by

$$W = \text{Tr}[H_1\rho_1] - \text{Tr}[H_0\rho_0] \quad (73)$$

$$\Delta A = W - \text{Tr}[(H_1 - H_0)\tilde{\rho}_0] \quad (74)$$

An explicit cyclic Hamiltonian capable of extracting the available energy is given (for $0 < t < \tau$) by:

$$H(t) = H_0 \cos\left(\frac{2\pi t}{\tau}\right) - \frac{2i\hbar}{\tau} \sin^2\left(\frac{\pi t}{\tau}\right) \ln \left[\sum_j |E_j\rangle \langle \Lambda_j| \right] \quad (75)$$

We will note the following in passing: that if the energy spectrum is bounded from above, then there is also *maximum* amount of work that may be unitarily performed *upon* the system, and a set of distributions for which that maximum is zero. These distributions have the property:

$$p_m \leq p_n \Leftrightarrow E_m \leq E_n \quad (76)$$

Unless otherwise stated, we will assume that the energy spectrum is not bounded from above, in which case these distributions will not have finite mean energy, and we will not consider them.

4.3 Interacting systems

We now move on to the situation where we have two systems that are allowed to interact for a period of time, so that $H(t) = H_1 \otimes I_2 + I_1 \otimes H_2 + V_{12}$. The combined system is isolated, except through the variation of the Hamiltonian.

First we have

$$\frac{\partial \langle H \rangle_\rho}{\partial t} = \frac{\partial \langle H_1 \rangle_{\rho_1}}{\partial t} + \frac{\partial \langle H_2 \rangle_{\rho_2}}{\partial t} + \frac{\partial \langle V_{12} \rangle_\rho}{\partial t} \quad (77)$$

$$= \left\langle \frac{\partial H}{\partial t} \right\rangle_\rho \quad (78)$$

$$= \left\langle \frac{\partial H_1}{\partial t} \right\rangle_{\rho_1} + \left\langle \frac{\partial H_2}{\partial t} \right\rangle_{\rho_2} + \left\langle \frac{\partial V_{12}}{\partial t} \right\rangle_\rho \quad (79)$$

with the middle line because the combined system is not interacting with any third system. We should not be surprised to see that the rate at which the mean energy of the combined system

changes, is equal to the mean of the rate at which work is performed upon the subsystems and the interaction between them.

We also have

$$i\hbar \frac{\partial \langle H_1 \rangle_{\overline{\rho_1}}}{\partial t} = i\hbar \left\langle \frac{\partial H_1}{\partial t} \right\rangle_{\overline{\rho_1}} + Q[H_1] \quad (80)$$

$$i\hbar \frac{\partial \langle H_2 \rangle_{\overline{\rho_2}}}{\partial t} = i\hbar \left\langle \frac{\partial H_2}{\partial t} \right\rangle_{\overline{\rho_2}} + Q[H_2] \quad (81)$$

$$i\hbar \frac{\partial \langle V_{12} \rangle_{\rho}}{\partial t} = i\hbar \left\langle \frac{\partial V_{12}}{\partial t} \right\rangle_{\rho} - Q[H_1] - Q[H_2] \quad (82)$$

where for convenience we define

$$Q[H_1] = \left\langle [H_1, V_{12}]_- \right\rangle_{\rho} = \sum_n i\hbar \frac{\partial p(\alpha_n)}{\partial t} \langle \alpha_n | H_1 | \alpha_n \rangle + \left\langle [H_1, \Theta_1]_- \right\rangle_{\overline{\rho_1}} \quad (83)$$

$$Q[H_2] = \left\langle [H_2, V_{12}]_- \right\rangle_{\rho} = \sum_n i\hbar \frac{\partial p(\beta_n)}{\partial t} \langle \beta_n | H_2 | \beta_n \rangle + \left\langle [H_2, \Theta_2]_- \right\rangle_{\overline{\rho_2}} \quad (84)$$

$$(85)$$

with

$$\overline{\rho_1} = \sum_n p(\alpha_n, t) |\alpha_n(t)\rangle \langle \alpha_n(t)| = \text{Tr}_2 [\rho(t)] \quad (86)$$

$$\overline{\rho_2} = \sum_n p(\beta_n, t) |\beta_n(t)\rangle \langle \beta_n(t)| = \text{Tr}_1 [\rho(t)] \quad (87)$$

and Θ_1 and Θ_2 are defined, as in Section 2.2, as the Hamiltonian operators

$$|\alpha_n(t)\rangle = \Upsilon_{\alpha}(t) |\alpha_n(0)\rangle \quad (88)$$

$$i\hbar \frac{\partial \Upsilon_{\alpha}(t)}{\partial t} = \Theta_1(t) \Upsilon_{\alpha}(t) \quad (89)$$

$$|\beta_n(t)\rangle = \Upsilon_{\beta}(t) |\beta_n(0)\rangle \quad (90)$$

$$i\hbar \frac{\partial \Upsilon_{\beta}(t)}{\partial t} = \Theta_2(t) \Upsilon_{\beta}(t) \quad (91)$$

$$(92)$$

The term $Q[H_1]$ clearly represents the mean rate at which energy is flowing into system 1, in addition to work being performed upon it, and similarly for $Q[H_2]$ and system 2. Remember also that if any two of H_1 , Θ_1 and $\overline{\rho_1}$ commute, the commutator term is zero.

We will now consider some simplifying conditions.

1. Constant interaction potential

If the only work being performed upon the joint system is through H_1 and H_2 , then $\frac{\partial V_{12}}{\partial t} = 0$:

$$i\hbar \frac{\partial \langle V_{12} \rangle_{\overline{\rho}}}{\partial t} + Q[H_1] + Q[H_2] = 0 \quad (93)$$

We now use the notation

$$\Delta X(t) = \int_0^t \frac{\partial \langle X \rangle_{\Omega}}{\partial t} dt = \langle X(t) \rangle_{\Omega(t)} - \langle X(0) \rangle_{\Omega(0)} \quad (94)$$

$$D[X(t)] = \int_0^t \left\langle \frac{\partial X(t)}{\partial t} \right\rangle_{\Omega(t)} dt \quad (95)$$

to consider how the mean energy of the systems change after a finite period of interaction. ΔH gives the change in the mean energy of the system over the course of the interaction, and $D[H]$ gives the mean work performed upon the system.

If the interaction term is constant in time, then

$$\Delta V_{12} + \int_0^t Q[H_1] dt + \int_0^t Q[H_2] dt = 0 \quad (96)$$

2. Finite interaction duration

We now suppose that the systems are initially separated so that $\text{Tr}[V_{12}(0)\rho(0)] = 0$ and that at time t they have been separated⁵ again $\text{Tr}[V_{12}(t)\rho(t)] = 0$.

$$\Delta Q = \int_0^t Q[H_1] dt = - \int_0^t Q[H_2] dt \quad (97)$$

$$\Delta H_1 = D[H_1] + \Delta Q \quad (98)$$

$$\Delta H_2 = D[H_2] - \Delta Q \quad (99)$$

ΔQ is the mean flow of energy between the two systems, during the interaction.

3. No change to second system

Finally we consider the effect of $\frac{\partial H_2}{\partial t} = 0$:

$$D[H_1] = \Delta H_1 - \Delta Q \quad (100)$$

$$\Delta H_2 = -\Delta Q \quad (101)$$

The interaction with the second system can allow energy to flow from system 2 into system 1. If the work done on system 1 is negative, $D[H_1] < 0$, the energy flow can be extracted. This can still be true if the variation in H_1 is cyclic, and even if $\Delta H_1 = 0$.

4.3.1 Completely passive distributions

We complete the notion of adiabatic availability by noting the need for a stronger notion than passivity is required if composite systems are considered. Let us consider a joint system, consisting of a joint Hamiltonian:

$$H_{12} = H_1 \otimes I_2 + I_1 \otimes H_2 \quad (102)$$

and a joint density matrix

$$\rho_{12} = \rho_1 \otimes \rho_2 \quad (103)$$

such that

$$H_1 = \sum_n E_n |E_n^{(1)}\rangle \langle E_n^{(1)}| \quad (104)$$

$$H_2 = \sum_n E_n |E_n^{(2)}\rangle \langle E_n^{(2)}| \quad (105)$$

$$\rho_1 = \sum_n p_n |E_n^{(1)}\rangle \langle E_n^{(1)}| \quad (106)$$

$$\rho_2 = \sum_n p_n |E_n^{(2)}\rangle \langle E_n^{(2)}| \quad (107)$$

⁵The moving of the systems can be achieved by variations in the internal Hamiltonians of each, so this does not conflict with $\frac{\partial V_{12}}{\partial t} = 0$.

Even if ρ_1 is a passive distribution (and, by construction, so will ρ_2 be), the combined density matrix ρ_{12} may not be a passive distribution.

To show this, we need only consider three energy levels, and their probabilities:

$$E_1 < E_2 < E_3 \quad (108)$$

$$p_1 > p_2 > p_3 \quad (109)$$

For the joint system to be passive it is necessary that

$$(2E_2 - E_1 - E_3)((p_2)^2 - p_1 p_3) < 0 \quad (110)$$

It is a simple matter to find values⁶ for which this fails and equally easy to find values⁷ for which this holds.

If a product of 2 equivalent passive systems, is passive, then the distribution may be termed 2-passive. Similarly, if a product of N equivalent passive systems is passive, then the distribution may be termed N -passive. A completely passive distribution (equivalent to the mutual stable equilibrium of [HG76]) is one that is N -passive, for all finite N .

The necessary and sufficient condition for N -passivity is that, for all combinations of natural numbers $\{a_i\}$ and $\{b_j\}$ such that

$$\sum_i a_i = \sum_j b_j = N \quad (111)$$

then

$$\left(\sum_i a_i E_i \leq \sum_j b_j E_j \right) \iff \left(\prod_i p_i^{a_i} \geq \prod_j p_j^{b_j} \right) \quad (112)$$

To simplify this, consider just three levels, $E_i < E_j < E_k$, and $b_j = N$. It is necessary that either

$$\begin{aligned} NE_j &\leq (N - n)E_i - nE_k \\ (p_j)^N &\geq (p_i)^{(N-n)}(p_k)^n \end{aligned} \quad (113)$$

or

$$\begin{aligned} NE_j &\geq (N - n)E_i - nE_k \\ (p_j)^N &\leq (p_i)^{(N-n)}(p_k)^n \end{aligned} \quad (114)$$

for $0 < n < N$.

Now as $NE_i < NE_j < NE_k$ and $(p_i)^N > (p_j)^N > (p_k)^N$, there must exist real numbers $0 < l_{(ijk)}, m_{(ijk)} < N$ such that

$$\begin{aligned} NE_j &= (N - l_{(ijk)})E_i - l_{(ijk)}E_k \\ (p_j)^N &= (p_i)^{(N-m_{(ijk)})}(p_k)^{m_{(ijk)}} \end{aligned} \quad (115)$$

⁶Consider

$$\begin{aligned} E_1 &= 1 & E_2 &= 3 & E_3 &= 4 \\ p_1 &= 1/2 & p_2 &= 1/3 & p_3 &= 1/6 \end{aligned}$$

Energy may be extracted by swapping the $|E_1 E_3\rangle$ and the $|E_2 E_2\rangle$ states.

⁷ $E_2 = 2$

For the system to be N -passive, $l_{(ijk)}$ and $m_{(ijk)}$ cannot be separated by any integers (as any such integer will yield an n for which the N -passive conditions fail). This must hold for all (ijk) triples of energy levels.

If we rewrite the above equations as

$$l_{(ijk)} = N \frac{E_j - E_i}{E_k - E_i} \quad (116)$$

$$m_{(ijk)} = N \frac{\ln(p_i) - \ln(p_j)}{\ln(p_i) - \ln(p_k)} \quad (117)$$

then

$$l_{(ijk)} - m_{(ijk)} = N \left(\frac{E_j - E_i}{E_k - E_i} - \frac{\ln(p_i) - \ln(p_j)}{\ln(p_i) - \ln(p_k)} \right) \quad (118)$$

Unless

$$\frac{E_j - E_i}{E_k - E_i} = \frac{\ln(p_i) - \ln(p_j)}{\ln(p_i) - \ln(p_k)} \quad (119)$$

it is clear that if N becomes sufficiently large then $|l_{(ijk)} - m_{(ijk)}| > 1$. When this happens the combined distribution is no longer passive, as there must exist an integer n between $l_{(ijk)}$ and $m_{(ijk)}$.

To be completely passive, it must be the case that for each triple $l_{(ijk)} = m_{(ijk)}$. This leads to

$$\frac{\ln(p_i/p_j)}{E_j - E_i} = \frac{\ln(p_i/p_k)}{E_k - E_i} \quad (120)$$

For this to hold for any triplet (ijk) of energy levels, then

$$\frac{\ln(p_i/p_j)}{E_j - E_i} = \beta \quad (121)$$

where β is a constant. Further rearranging shows

$$\ln(p_i) + \beta E_i = \ln(p_j) + \beta E_j = \ln \lambda \quad (122)$$

where λ is also a constant, giving⁸:

$$p_i = \lambda e^{-\beta E_i} \quad (123)$$

for all i . It is a simple matter to verify this distribution is sufficient for N -passivity. As the value of N has disappeared, it is apparent that the canonical distribution must be N -passive, for all any N . It follows that the canonical distribution is the unique, completely passive distribution, for separable Hilbert spaces[PW78, Len78, Sew80].

4.4 Summary

Does much of the above seem somewhat obvious? We should hope so! All we have done is to apply the normal rules of probability theory to Hamiltonian evolutions. We have derived average terms for the rate of change of energy, rate of work and the flow of energy between two interacting systems. We need make no reference to thermodynamic concepts to do this. There is no need to introduce approximations and the results apply to systems with any (finite) number of degrees of freedom.

⁸Note: passivity requires $\beta > 0$.

Remarkably, we have shown how there is maximum amount of energy, the adiabatic availability of the system, that can be extracted as work from an isolated system, in a specific type of cyclic process. Not all of the energy of a system is available for work. This conclusion can be drawn without needing to invoke notions of entropy or consider thermal heat baths or engines operating between them.

Most remarkably we have a concept of passivity, that seems similar to thermal equilibrium, and a stronger concept of complete passivity, or mutual stable equilibrium, and the only completely passive distribution is the canonical distribution! Yet we have at no point referred to any thermal concepts, whether entropy, temperature or thermal equilibrium.

There may be disagreement over when a probabilistic statement can be justified. There may be disagreement over what such a statement means. There may even be disagreement over what the value of the probability is. Whenever probabilistic statements are justified, the results given here follow.

5 Statistical Temperature

Having established the rules of statistical mechanics, we now need to see if it can account for thermal phenomena. We wish to avoid, as far as possible, assuming any of the structure of thermodynamics, and instead focus upon the physical phenomena. It is tempting to go from complete passivity to a Large Completely Passive Assembly, and then identify this with an environmental heat bath. We will continue to resist temptation! We still have not yet justified that the physical systems we characterise as thermal states are actually canonical distributions.

To do this, we will deduce, from a set of observations, that there is only one possible way to represent thermal states in the context of statistical mechanics and that is the canonical distribution. No reference to ideas of entropy, heat baths, approaches to equilibrium, or information theory, will need to be used. The analysis here was inspired largely by [Szi25], although the presentation differs quite significantly.

5.1 Some properties of temperature

Statistical mechanics has a far broader scope than thermal phenomena. To see how statistical mechanics deals with thermal phenomena we must first identify what thermal phenomena are, and how this restricts the description of the systems to which we wish to apply the methods of statistical mechanics. We do not derive the concept of temperature. Instead we consider temperature an empirically observed phenomena and ask what the theoretical description of such phenomena could be. What are the empirical properties we know about these thermal systems, and what constraints does this lay upon what physical states can represent them?

Our approach will be to start by examining the phenomena of temperature, taking it for granted that we have some notion of temperature from our experience of things being *hot* and *cold*. We will not need to consider what it means for one system to be *hotter* than another, only what it means for two systems to be at the same temperature as each other.

We will state the following properties of two systems that are at the same temperature:

1. No spontaneous flow of energy.

If two systems in isolation, are at the same temperature, then if they interact with each other there can be no *mean* flow of energy between them. Energy may be exchanged in individual systems, as fluctuations, but the expectation value for the exchange must be zero.

2. Composition.

Temperature is not changed by combining systems at the same temperature. When two systems are each individually at the same temperature as each other, then the joint system that is formed by combining those two systems, is a system at the same temperature.

These two observations are all we need to derive thermal physics from statistical mechanics. We will also show that the composition property may be replaced by the following two conditions:

2. (a) Transitivity.

Temperature is transitive between systems. When two systems are each individually at the same temperature as a third system, then they are at the same temperature as each other.

(b) Universality.

The property of being at a *particular* finite temperature, can hold for every possible system. So, for any given Hamiltonian, there exists at least one distribution that corresponds to each temperature.

5.2 Deriving the temperature distribution

We wish to regard the previous statements as providing a set of empirical observations that we are going to use to deduce how thermal states needs to be treated in statistical mechanics.

1. No spontaneous flow of energy.

First we must clarify what is the observed phenomena we are proposing, and secondly, how that can be represented.

In general, when two objects, initially non-interacting, are brought into contact, and allowed to interact through that contact, when they are separated their states have changed. Careful calorimetry experiments, based upon the work required to effect the equivalent changes to those systems, when isolated from each other, allows us to identify a quantity of energy that was exchanged between the two systems.

When systems are at the same temperature, the quantity of energy exchanged is zero. This needs two qualifications. When the measurements are sufficiently sophisticated to include fluctuation phenomena, the energy exchanged in any one instance, of contact between two systems, may be non-zero. The energy exchange is still zero *on average*. Also, we must exclude interactions that can cause chemical or nuclear reactions. To do this we require the output density matrices to have non-zero eigenvalues only in those regions of state space for which the input density matrices have non-zero eigenvalues.

Before contact, the systems are separated, and so described by a product density matrix with a non-interacting Hamiltonian:

$$\begin{aligned}\rho_0 &= \rho_1 \otimes \rho_2 \\ H_0 &= H_1 \otimes I_2 + I_1 \otimes H_2\end{aligned}\tag{124}$$

In principle we could allow an interaction Hamiltonian V_{12} subject to $\text{Tr}[V_{12}\rho_0] = 0$.

The two systems are now brought into contact. This can happen in two possible ways: the interaction Hamiltonian V_{12} is changed, so it becomes non-zero for ρ_0 ; or at least one of the system Hamiltonians is changed so that ρ_0 itself evolves into a state ρ for which $\text{Tr}[V_{12}\rho] \neq 0$.

We will represent both cases by simply assuming overall a time varying Hamiltonian, $H(t)$, such that $H(t) = H_0 \forall t < 0$. As the interaction is of a time limited duration, we also require there exist a time τ for which $H(t) = H_0 \forall t > \tau$.

We now want to focus on the concept of a *spontaneous* flow. We cannot take this to mean in the absence of all interventions, as we are having to intervene to bring the systems into contact, then separate them. This involves a time variation in the Hamiltonian, and the possibility of work being performed upon the system. For a flow of energy to be spontaneous, therefore, we add the restriction that the net work performed upon the joint system, over the course of the interaction, be zero.

We can summarise this as follows:

$$\begin{aligned} U &= e^{i \int_0^\tau H(t)} \\ \rho_\tau &= U \rho_0 U^\dagger \\ W &= \text{Tr} [H_0 (\rho_\tau - \rho_0)] \\ \Delta E_1 &= \text{Tr} [H_1 \otimes I_2 (\rho_\tau - \rho_0)] \\ \Delta E_2 &= \text{Tr} [I_1 \otimes H_2 (\rho_\tau - \rho_0)] = W - \Delta E_1 \end{aligned} \tag{125}$$

A necessary condition for ρ_1 and ρ_2 be at the same temperature as each other is that, for all $H(t)$ such that $W = 0$, then $\Delta E_1 = 0$. In other words, if the two systems are at the same temperature, then provided no work is performed upon the joint system, there can be no exchange of energy between the two systems.

We can also see that, for this condition to be met, it is necessary to consider only the overall unitary evolutions U , and not the detailed interaction $H(t)$. If we rewrite the condition as: for ρ_1 and ρ_2 be at the same temperature as each other, then for all U for which $W = 0$, it must be the case that $\Delta E_1 = 0$; we can immediately note that the system ρ_0 must be a passive system.

If ρ_0 is not a passive system, then it is possible to extract its adiabatic availability as work. We can then apply that same quantity of work, to either system, in isolation. The net work is zero, but energy can be exchanged. It follows that if ρ_0 is not passive, there exists a unitary evolution that violates the conditions for ρ_1 and ρ_2 to be at the same temperature, as a Hamiltonian interaction may always be constructed to implement the unitary evolution.

2. Composition.

If two systems are individually at the same temperature T , then the combined system is also at that same temperature T . This is a surprising property. It is not directly deducible from the more familiar transitivity property of temperature, but certainly embodies one of our intuitive notions of what it means for two systems to be at the same temperature.

Let us express the concept of ‘being at the same temperature’ as a relationship ‘ \sim ’, so that $\rho_1 \sim \rho_2$ means ρ_1 and ρ_2 are at the same temperature⁹. The compositional property states:

$$\rho_1 \sim \rho_2 \Rightarrow \rho_1 \sim \rho_1 \otimes \rho_2 \tag{126}$$

We also know, from the first property, that if $\rho_1 \sim \rho_2$, then $\rho_1 \otimes \rho_2$ is passive. As $\rho_1 \sim \rho_1$, from induction it follows that $\rho_1 \otimes^N \rho_1$ is passive, for all N . It follows for ρ_1 to be a temperature state, that it must be completely passive, and hence a canonical distribution.

⁹The relationship is clearly symmetric, so that $\rho_1 \sim \rho_2 \Leftrightarrow \rho_2 \sim \rho_1$ and reflexive, so that $\rho_1 \sim \rho_1$.

This compositional property of thermal states is rarely emphasised, although it plays a very strong role in our intuitive sense of what is required of a state, for it to be thermal. The transitive property of temperature is more usually encountered. Can transitivity be used to deduce the canonical distribution?

2. (a) Transitivity

The transitivity of temperature is closely related to the operational requirement that any two systems, when usable as thermometers, must agree when systems are at the same temperature. When applied to statistical states, it defines a necessary, but not sufficient, requirement for the states to be considered at the same temperature.

The first requirement gives us a necessary condition for ρ_1 and ρ_2 to be at the same temperature: that $\rho_1 \otimes \rho_2$ be passive. Suppose there is a third system ρ_3 . The fact that $\rho_1 \otimes \rho_3$ and $\rho_2 \otimes \rho_3$ may both be passive is not sufficient to ensure $\rho_1 \otimes \rho_2$ is passive. Transitivity is, therefore, a further restriction.

However, if $\rho_1 \otimes \rho_2$ is not passive, we are unable to say whether it is ρ_1 or ρ_2 (or neither) that could still be regarded as being at the same temperature as ρ_3 . All that we can say is that, for a collection of distributions, $\{\rho_1, \dots, \rho_n\}$, to be all at the same temperature, T , it is necessary that every combination $\rho_i \otimes \rho_j$ be a passive distribution. If we introduce a new distribution, which is only jointly passive with *some* of the original collection, is it the new system that is not at the same temperature, or was it our original collection, that was not a true collection of distributions at the same temperature?

(b) Universality We now introduce the assumption that temperature be *universal*. By this we mean that, for any system Hamiltonian, and any finite temperature, there is at least one distribution over the energy spectrum of that Hamiltonian, that corresponds to that temperature.

In other words, under the assumption of universality, given a collection, $\{\rho_1, \dots, \rho_n\}$, of distributions at the same temperature, and any Hamiltonian, H_{n+1} , of a new system, then it must always be possible to find a distribution ρ_{n+1} over the new system, such that $\rho_i \otimes \rho_{n+1}$ is passive, for all $1 \leq i \leq n$.

We can use these properties to establish that the ratio of the probabilities of any two energy levels must be a single valued function of their energy difference, and the temperature.

First suppose we have a given system, with two energy levels separated by the gap $E_1 - E_0 = \Delta$, and the ratio of whose probabilities is given by $p_1/p_0 = \Pi$. If we consider two levels, i and j , of any other system, then comparison of the $|E_1 E_i\rangle$ and $|E_0 E_j\rangle$ levels yields:

$$E_i - E_j \geq \Delta \Leftrightarrow \frac{p_i}{p_j} \leq \Pi \quad (127)$$

Now we consider all Hamiltonians that contain levels with the energy gap Δ . This will yield maximum and minimum values of Π for that energy gap, and so:

$$\begin{aligned} E_i - E_j \geq \Delta &\Leftrightarrow \frac{p_i}{p_j} \leq \Pi_{min} \\ E_i - E_j \leq \Delta &\Leftrightarrow \frac{p_i}{p_j} \geq \Pi_{max} \end{aligned} \quad (128)$$

As we can do this for all values of Δ , we generate two functions $\Pi_{max}(\Delta)$ and $\Pi_{min}(\Delta)$. A little thought shows, that given for all $\Delta' \geq \Delta$, then $\Pi_{max}(\Delta') \leq \Pi_{min}(\Delta)$, these functions must both be piecewise continuous.

We next demonstrate that $\Pi_{max}(\Delta) = \Pi_{min}(\Delta)$. Consider a Hamiltonian with four non-degenerate energy levels, for which the energy gaps between the lowest and the three higher are $\Delta - \delta_1$, $\Delta - \delta_2$ and $\Delta + \delta_3$, respectively, such that $\delta_1 > \delta_2$ and $\delta_1, \delta_2, \delta_3 > 0$. The inverse ratio of the probability of the lowest of the energy level, to the $\Delta - \delta_1$ energy level, is Π_1 , to the $\Delta - \delta_2$ energy level, is Π_2 , and to the $\Delta + \delta_3$ energy level, is Π_3 .

Now consider the product of two systems with the four energy levels. Comparing the $|E_2, E_2\rangle$ with the $|E_1, E_3\rangle$ levels, if $\delta_3 - \delta_1 \geq 2\delta_2$ then $(\Pi_2)^2 \leq \Pi_1 \Pi_3$.

By the definition of $\Pi_{max}(\Delta)$ and $\Pi_{min}(\Delta)$, as we vary through Hamiltonians so that $\delta_1, \delta_2, \delta_3 \rightarrow 0$, we have

$$\begin{aligned}\Pi_1, \Pi_2 &\rightarrow \Pi_{max}(\Delta) \\ \Pi_3 &\rightarrow \Pi_{min}(\Delta)\end{aligned}\tag{129}$$

Provided we maintain $\delta_3 - \delta_1 \geq 2\delta_2$, such as by $\delta_2 = \frac{1}{4}(\delta_3 - \delta_1)$, then

$$\Pi_{max}(\Delta)^2 \leq \Pi_{max}(\Delta)\Pi_{min}(\Delta)\tag{130}$$

which gives $\Pi_{max}(\Delta) \leq \Pi_{min}(\Delta)$, but $\Pi_{max}(\Delta) \geq \Pi_{min}(\Delta)$, by definition, so $\Pi_{max}(\Delta) = \Pi_{min}(\Delta) = \Pi(\Delta)$.

We now have demonstrated that the property of universality of temperature, requires that there exists, for each value T , of temperature, a function $\Pi_T(\Delta)$, such that

$$\frac{p_i}{p_j} = \Pi_T(E_i - E_j)\tag{131}$$

It is a simple matter to deduce the unique function that satisfies this. Considering a third level

$$\frac{p_k}{p_j} = \Pi_T(E_k - E_j) = \frac{\Pi_T(E_i - E_j)}{\Pi_T(E_i - E_k)}\tag{132}$$

Writing $\Delta_1 = E_k - E_j$ and $\Delta_2 = E_i - E_k$, gives

$$\Pi_T(\Delta_1 + \Delta_2) = \Pi_T(\Delta_1)\Pi_T(\Delta_2)\tag{133}$$

We find a variation on the Darboux relationship [Dar80], which has the solution:

$$\frac{p_i}{p_j} = e^{-\beta(T)(E_i - E_j)}\tag{134}$$

We can rearrange this

$$p_i e^{\beta(T)E_i} = p_j e^{\beta(T)E_j} = \lambda\tag{135}$$

where λ is a constant, which by normalisation of the probabilities, is

$$\lambda = \frac{1}{\sum_i e^{-\beta(T)E_i}}\tag{136}$$

Transitivity therefore yields the canonical distribution, but only if we supplement it with the requirement that temperature be universal.

5.3 Comments

The concept of passivity is clearly closely related to the concept of equilibrium. However, we have not made any assumptions regarding whether systems, not in equilibrium, must evolve into a state of equilibrium, or whether systems, in equilibrium, may spontaneously be found out of equilibrium. The temporal asymmetry associated with the concept of equilibrium[BU01], which is so problematical for the relationship of statistical mechanics to thermal physics, has not been assumed.

It appears we do not need to assume that isolated systems tend to equilibrium to understand what a *thermal* state must be. The only sense of equilibrium that we may be argued to have used here, is a sense in which two states at the same temperature may be regarded as being in equilibrium with each other. This is a relationship between systems, not property of individual systems.

Having said that, if the result of thermalising a system did not lead to a passive distribution, then clearly we could create perpetual motion: simply isolate the thermalised system, extract the available energy, then restore thermal contact and allow the system to return to the thermalised state.

Another sense of equilibrium, that a distribution is in equilibrium if it is constant in time, also leads to the conclusion that the distribution must be diagonalised in the energy eigenbasis. Of course, we have seen that the concept of passivity is also sufficient to deduce the density matrix diagonalises the energy eigenbasis.

That the compositional property rules against the microcanonical distribution was noted, in passing, by Gibbs[Gib02][pg. 170-4]. It is key (although not obviously so) to Szilard's derivation of the canonical distribution for classical systems[Szi25].

It is the factorisability of the joint probability distribution of the combined state that leads uniquely to the canonical distribution. This is deeply related to the development of the statistical mechanical account of thermal phenomena. Non-extensive entropies must, at least implicitly, deny this property. Both the extensivity of Gibbs entropy and the additivity of Shannon information are, formally, closely related to this. The extensivity of entropy is a somewhat abstract concept, which has something of the status of convention even in classical phenomenological thermodynamics. Shannon information has no obvious a priori relationship to thermal phenomena and has played no role in this derivation. The compositional property of temperature is a verifiable physical property of thermal states.

5.4 The Ideal Gas Scale

The temperature *scale* is largely a matter of convention. Consistency amongst different operationally defined temperatures requires that any two thermal states considered to be at the same temperature with respect to one scale, are at the same temperature with respect to any other scale. It is usually also assumed that the primitive ordering of *hotter than/colder than* is also preserved across all temperature scales. This would mean that any temperature scale can be expressed as a monotonic function of any other scale.

We could choose to use $\beta(T)$ as the definition of our statistical temperature scale. Provided β is a single valued function, it satisfies the consistency requirement. To verify the ordering relationship, we will identify a particular operationally defined temperature scale and find how $\beta(T)$ varies with that.

We will make the choice of the ideal gas scale. It is empirically observed that, for a number of

gases, the relationship:

$$PV = NRT \quad (137)$$

appears to hold, where the number of moles of the gas is N and R is the molar gas constant. It is hypothesised this holds exactly for *ideal* gases.

Standard textbook analysis of a canonically distributed system, gives us the result that an ideal n quantum gas confined to a box of volume V , exerts a mean pressure P on the walls of the box of:

$$PV\beta(T) = n \quad (138)$$

The Boltzmann constant $k = RN/n$ gives

$$\beta(T) = \frac{1}{kT} \quad (139)$$

As this is a single valued, monotonic function of T , it follows $\beta(T)$ is a good temperature scale, provided the ideal gas scale, T , is a good temperature scale.

6 Statistical Thermal States

We have identified thermal states as uniquely represented in statistical mechanics by canonical probability distributions. The canonical probability distribution is characterised by a single parameter, $\beta(T)$, which can be related to the reciprocal of the ideal gas scale. We will now consider what we can deduce, solely from the identification of thermal states as canonical probability distributions, using the techniques of statistical mechanics.

6.1 Mean flow of energy

We can state immediately the consequence of Equation 44:

$$\Delta H_1 (\beta_2 - \beta_1) \geq 0 \quad (140)$$

If two thermal states interact, with *different* parameters β_1 and β_2 , then if $\beta_1 > \beta_2$, the mean flow of energy, $\Delta H_1 \leq 0$, can only be from system 2 to system 1.

6.2 Thermal cycles

Next consider a system, with an arbitrary probability distribution, $\rho^{(0)}$, initially uncorrelated or interacting with any other system. The system is now brought into successive contact with a series of systems in thermal states, where the state of system i is parameterised by β_i . After each contact has ceased, the expectation value for the interaction energy with the i^{th} system is zero. The internal Hamiltonians for the canonical states systems are constant in time.

Let $\rho^{(i)}$ be the marginal probability distribution of the system after interacting with the i^{th} thermal system. Let $\rho_i(\beta_i)$ be the initial probability distribution of the i^{th} thermal system, and ρ'_i be the marginal probability distribution afterwards. Let ΔH_i represent the mean energy flow into the i^{th} thermal system. We do not assume any of the systems are canonically distributed after the interaction.

Now, purely from the mathematical properties of canonical distributions (Section 2) we can state:

$$G[\rho^{(i-1)}] + G[\rho_i(\beta_i)] \geq G[\rho^{(i)}] + G[\rho'_i] \quad (141)$$

$$G[\rho'_i] - G[\rho_i(\beta_i)] \geq -\beta_i \Delta H_i \quad (142)$$

Adding these together and summing over all interactions we get

$$G[\rho^{(0)}] - G[\rho^{(f)}] \geq - \sum_i \beta_i \Delta H_i \quad (143)$$

from which it follows that, if the series of interactions is such that it returns the systems final marginal probability distribution to its initial probability distribution $\rho^{(f)} = \rho^{(0)}$ then:

$$\sum_i \beta_i \Delta H_i \geq 0 \quad (144)$$

No physical interpretation need be placed upon the Gibbs-von Neumann measure G , to derive these results. We are deducing a property (Equation 144) of canonical distributions, under Hamiltonian evolution.

We have not needed to assume that the system Hamiltonian returns to it's initial value. If this is the case, the mean work performed over the course of the cycle is

$$\Delta W = \sum_i \Delta H_i \quad (145)$$

6.3 Statistical thermalisation

Now consider a system with an arbitrary probability distribution, $\rho^{(0)}$, initially uncorrelated or interacting with any other system, and a Hamiltonian H . The system is now brought into successive contact with a series of systems in thermal states, where each system has the same parameter β . Let $\rho^{(i)}$ be the marginal probability distribution of the system after interacting with the i^{th} thermal system, and let $\rho(\beta)$ be the thermal state for the system with parameter β .

$$G[\rho(\beta)] + \beta \langle H \rangle_{\rho(\beta)} \leq G[\rho^{(i+1)}] + \beta \langle H \rangle_{\rho^{(i+1)}} \leq G[\rho^{(i)}] + \beta \langle H \rangle_{\rho^{(i)}} \leq G[\rho^{(0)}] + \beta \langle H \rangle_{\rho^{(0)}} \quad (146)$$

As each equality holds only if the system is canonically distributed $\rho(\beta)$ we conclude that, if there is no physical cause that prevents it, a system with any arbitrary probability distribution can be brought arbitrarily close to a canonical probability distribution, with the parameter β , by a sufficiently large number of such contacts. The system becomes thermalised.

Possible physical causes that prevent complete thermalisation include:

1. Transitions are not permitted between different regions of the state space. Let the different regions of state space be represented by the complete set of non-overlapping projectors K_i onto those regions, the partial thermalisation of the density matrix ρ , will be:

$$\rho'(\beta) = \sum_i \text{Tr}[K_i \rho K_i] \frac{e^{-\beta K_i H K_i}}{\text{Tr}[e^{-\beta K_i H K_i}]} \quad (147)$$

2. Only part of the region of the state space represents the system being in thermal contact (i.e. the interaction Hamiltonian is zero for some portion of the system state space) and there are no transitions out of that region. If K_α projects onto the isolated region, and K_β onto the thermal contact region, partial thermalisation will lead to:

$$\rho'(\beta) = K_\alpha \rho K_\alpha + \text{Tr}[K_\beta \rho K_\beta] \frac{e^{-\beta K_\beta H K_\beta}}{\text{Tr}[e^{-\beta K_\beta H K_\beta}]} \quad (148)$$

At the risk of getting repetitive, we restate: no physical interpretation is placed upon the Gibbs measure G to derive these results. It is used simply to establish general mathematical properties of the evolution of distributions under Hamiltonian evolutions and of interactions with thermal states. The properties of these interactions can be understood without needing to physically interpret the Gibbs measure. They are properties of Hamiltonian evolutions.

6.4 Heat Baths

It will now be convenient to identify heat baths. A heat bath is simply a large system, with many degrees of freedom, in a thermal state. With many degrees of freedom it can be treated as having a large number of subsystems. No work is ever performed upon a heat bath.

When a system interacts with a heat bath, it generally interacts only with one of the subsystems. What happens following that depends upon the details of the heat bath, the interactions between the subsystems and whether continued interaction with the heat bath involves continued interaction with the same, or a different, subsystem. We will use the symbol ΔQ to refer to mean energy flows into a heat bath, and will refer to these as mean heat exchanges.

6.4.1 Ideal Heat baths

An ‘ideal’ heat bath, which is one for which the subsystems are non-interacting, and an individual subsystem is never encountered twice. All the subsystems are canonically distributed with the same β parameter, and it is assumed there are no internal microscopic correlations. This means a system brought into contact with an ideal heat bath experiences a succession of contacts with independent canonically distributed systems at the same β parameter. It will become thermalised. An ideal heat bath may be treated as a Large Uncorrelated Canonical Assembly (Section 2.5) which is identical to a Large Completely Passive Assembly. The interaction with each subsystem will be for a very short time¹⁰. From the completely passive properties of thermal systems, we can state immediately it is impossible to extract work from any number of ideal heat baths at the same temperature.

6.4.2 Real Heat baths

Of course, as soon as the systems have interacted, correlations develop and do not disappear. Subsystems of real heat baths interact with each other. Subsystems may be re-encountered.

To judge the consequences of these requires real models of physical heat baths. For example, one property of weakly interacting subsystems[Par89] is a tendency for correlations to become “spread out”, so that the correlation between the system and the heat bath subsystem is reduced by the weak interaction amongst the heat bath subsystems.

Real heat baths do not behave exactly as ideal heat baths. The properties we are going to derive based upon ideal heat baths will not, therefore, be strictly applicable to interactions with real heat baths. The extent to which the behaviour of real heat baths differs from that of ideal heat baths can only be decided by examining physical models of the real heat baths.

That real heat baths do not behave exactly as ideal heat baths is not a fundamental problem for statistical mechanics. Statistical mechanics should not be required to prove real heat baths behave as ideal heat baths - after all, they don’t! When considering real heat baths, with real physical interactions, statistical mechanics is required to accurately describe the actual behaviour of those

¹⁰Care needs to be taken regard a limiting case of infinitesimally short interactions or the quantum Zeno effect will prevent thermalisation at all.

real heat baths, including how they *deviate* from being ideal heat baths, given the appropriate description of the real physical interaction.

6.5 Statistically isothermal operations

We now consider the limiting cases of interactions with an ideal heat bath. When a thermal system, with internal Hamiltonian H is brought into contact with an ideal heat bath with a fixed β parameter, the system is kept in a thermalised state¹¹. The resulting canonical distribution gives a density matrix which is always diagonalised with respect to the system Hamiltonian. As the system Hamiltonian is varied, the mean work performed is

$$\Delta \langle W \rangle = \int_0^\tau \text{Tr} \left[\frac{\partial H}{\partial t} \frac{e^{-\beta H}}{\text{Tr}[e^{-\beta H}]} \right] dt \quad (149)$$

$$= \int_0^\tau \sum_n \frac{\partial E_n}{\partial t} \frac{e^{-\beta E_n}}{\sum_n e^{-\beta E_n}} dt \quad (150)$$

and the mean heat exchanged is

$$\Delta \langle Q \rangle = \int_0^\tau \sum_n E_n \frac{\partial}{\partial t} \left(\frac{e^{-\beta E_n}}{\sum_n e^{-\beta E_n}} \right) dt \quad (151)$$

The work may be re-expressed as

$$\Delta \langle W \rangle = -\frac{1}{\beta} \ln \left[\frac{Z(\tau)}{Z(0)} \right] \quad (152)$$

where

$$Z(t) = \text{Tr} [e^{-\beta H(t)}] \quad (153)$$

7 Statistical Entropy

The results of the previous section have not, at any point, depended upon the identification of $-G$ with thermodynamic entropy. The Gibbs-von Neumann measure of a distribution has been treated simply as a convenient calculation tool, and has not been attributed any physical significance. The “entropy-like” qualities of G that have been used are simply mathematical properties of any distribution function under Hamiltonian evolutions. No physical interpretation has been placed upon them, nor was needed to use them.

Nevertheless we have managed to derive the inequality

$$\sum_i \frac{\Delta Q_i}{T_i} \geq 0 \quad (154)$$

where Q_i is the mean heat flow, into a thermal system at temperature T_i , over a closed cycle. The mean work performed over the course of the cycle is

$$\Delta W = \sum_i \Delta Q_i \quad (155)$$

Consider a few special cases of this, for heat baths:

¹¹Provided the Hamiltonian is varied only slowly.

1. If there is a single heat bath:

$$\Delta Q \geq 0 \quad (156)$$

the mean flow of energy *must* be into the heat bath.

2. If there are two heat baths, and the mean work requirement for the process is zero, $\Delta Q_1 = -\Delta Q_2 = \Delta Q$:

$$\Delta Q \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \geq 0 \quad (157)$$

$\Delta Q > 0$ if and only if $T_1 \leq T_2$. The mean flow of heat into the first heat bath can be positive only if the first heat bath is colder than the second.

3. If there are two heat baths,

$$\frac{\Delta W}{\Delta Q_1} \leq 1 - \frac{T_2}{T_1} \quad (158)$$

Which (with due regard for changes in sign to both ΔW and ΔQ_1) shows the maximum efficiency, in terms of mean work extracted over mean heat extracted, for a heat engine.

7.1 Thermodynamic entropy

We will now, for the first time, consider phenomenological thermodynamics. The primitive exposition of the concept of thermodynamic entropy here clearly lacks the careful rigour of such works as [GB91, LY99] and indeed differs greatly from them. It is closer to such textbook expositions such as [Fer37, Adk68]. Our reasons for this are simple: it is not obvious what the statistical mechanical generalisation of thermodynamic entropy should be and there is no universal agreement on what properties of thermodynamic entropy are the ones to select in developing this generalisation (or even if such a generalisation is necessary). Our approach will be to focus upon the arguments that typically motivate supposing that there is such a thing as thermodynamic entropy in the first place and see how these arguments apply to statistical mechanics.

The three cases in the previous section may be compared to three versions of the Second Law of Thermodynamics

1. No process is possible whose sole result is the extraction of heat from a heat bath and its conversion into work.
2. No process is possible whose sole result is the transfer of heat from a colder to a hotter heat bath.
3. No process is possible whose sole result is the extraction of heat Q_1 from a heat bath at temperature T_1 and the deposit of heat Q_2 in a heat bath at temperature $T_2 < T_1$, extracting the remainder $W = Q_1 - Q_2$ with efficiency $\eta = W/Q_1$ greater than $1 - T_2/T_1$.

An equivalent expression of the Second Law would be:

4. No process is possible, whose sole result is the use of work to transfer heat between heat baths, such that the heat deposited in the n^{th} heat bath, at temperature T_n , is Q_n and

$$\sum_n \frac{Q_n}{T_n} < 0 \quad (159)$$

Now, the final expression leads to the following result:

If there exists a process, which takes a system from state A, to a system at state B, depositing heats $Q_m^{(1)}$ in heat baths at temperatures $T_m^{(1)}$, then there can be no process, which takes a system in state B, to a system in state A, depositing heat $Q_n^{(2)}$ in heat baths at temperatures $T_n^{(2)}$, unless

$$\sum_m \frac{Q_m^{(1)}}{T_m^{(1)}} + \sum_n \frac{Q_n^{(2)}}{T_n^{(2)}} \geq 0 \quad (160)$$

As this result must hold for *any* two states A and B in any combination of processes, this is equivalent to the statement:

There exists a single valued property, S , of a state such that, if there exists a process, which takes a system from state A, to a system at state B, depositing heats $Q_m^{(1)}$ in heat baths at temperatures $T_m^{(1)}$, then

$$S[B] - S[A] \geq - \sum_m \frac{Q_m^{(1)}}{T_m^{(1)}} \quad (161)$$

The value of this property S is not yet uniquely defined. There may be many functions which satisfy this requirement.

If there also exists a process, which takes a system from state B, to a system at state A, depositing heats $Q_n^{(1)}$ in heat baths at temperatures $T_n^{(1)}$, such that

$$\sum_m \frac{Q_m^{(1)}}{T_m^{(1)}} + \sum_n \frac{Q_n^{(2)}}{T_n^{(2)}} = 0 \quad (162)$$

then S is uniquely defined¹² by:

$$S[B] - S[A] = - \sum_m \frac{Q_m^{(1)}}{T_m^{(1)}} \quad (163)$$

Identifying the value of S for all states then requires us to find processes in both directions which are able to complete the cycle with the requisite minimal transfer of heat to heat baths.

If we can identify the value of S for all states then it follows

There is no process which takes a system from state A, to a system at state B, depositing heats $Q_m^{(1)}$ in heat baths at temperatures $T_m^{(1)}$, for which

$$S[B] + \sum_m \frac{Q_m^{(1)}}{T_m^{(1)}} < S[A] \quad (164)$$

and finally, if we identify the change in the value of S for a heat bath with Q/T , we get

There is no process for which

$$\sum \Delta S < 0 \quad (165)$$

The quantity S is the thermodynamic entropy of the state.

¹²Up to an additive constant, of course!

7.2 Statistical mechanical generalisation of thermodynamic entropy

The first thing we may wonder is whether there is any need to introduce the concept of a statistical mechanical entropy. The existence of the non-decreasing function of state is equivalent to the various operational statements of the second law, about the absence of certain kinds of processes. One of these statements must be introduced into the axiomatic structure of thermodynamics to be able to deduce results as, whichever statement is chosen as the appropriate second law axiom, otherwise it cannot be deduced.

For statistical mechanics, we *can* deduce the statistical equations from the properties of Hamiltonian dynamics, probability calculus and the existence of thermal states. There is no need to introduce a new axiom. Nevertheless, the tremendous utility of the thermodynamic entropy function in developing phenomenological thermodynamics should suggest to us that such a function may be useful. Perhaps it may be possible, in principle, to develop phenomenological thermodynamics without introducing an entropy function, but instead, for example, rely solely upon the Kelvin formulation of the second law, but it would seem needlessly difficult to do so.

If we decide to introduce such a function, let us consider the phenomenological laws which motivate introducing it. The first thing to note is that they are all *false*. It is possible to have processes whose sole result is to convert heat to work (just with probability less than one). It is possible to have processes whose sole result is to transfer energy from a colder to a hotter heat bath (just with probability less than one).

This has a profound consequence for the development of a statistical mechanical entropy. The justification for introducing entropy as a single valued property of state comes from Equation 160 above. This justification *does not hold* for microstates.

Hamiltonians exist which can transform any microstate into any other microstate, while extracting arbitrarily large amounts of heat from a heat bath and converting it into work, so long as we are prepared to accept an arbitrarily low probability of the process occurring. No single valued entropy function could be deduced from this attempt.

Attempting to fix this by demanding that the process can occur with certainty, we find that there is always some Hamiltonian evolution on the state space, which can perform a transformation between any two given microstates, without any exchange of energy with a heat bath. The same conclusion is reached even if we demand only that the *mean* transfer of heat to the heat baths be zero. The entropy difference between any two microstates is zero.

7.2.1 Defining the statistical mechanical entropy

The steps that might lead us to try to deduce the existence of an entropy function as a function of the microstate of a system are flawed. However, there was no reason to take those steps. The search for new axioms to introduce, to represent a statistical mechanical second law, is unnecessary. Statistical mechanics has already enabled us to deduce the property:

No process is possible, starting with any probability distribution over a system, whose sole result is to return the system to it's a marginal probability distribution equal to it's initial distribution, and to transfer mean quantities of energy ΔQ_i into systems initially uncorrelated and canonically distributed with parameters β_i , where

$$\sum_i \beta_i \Delta Q_i < 0 \quad (166)$$

Note that this deduction, as expressed, is a direct consequence of Hamiltonian dynamics and does not depend upon any identification of thermal states, temperatures or heat baths.

Accepting the identification of thermal states as canonical distributions, and the state of a system being here defined as a Hilbert space, Hamiltonian operator on that space and probability distribution over the space, it follows:

There exists a single valued property, S , of the states of systems such that, if there exists a process, which takes a system from state A, to a system at state B, depositing mean heats $Q_m^{(1)}$ in thermal systems at temperatures $T_m^{(1)}$, then

$$S[B] - S[A] \geq - \sum_m \frac{Q_m^{(1)}}{T_m^{(1)}} \quad (167)$$

We define this property as the statistical mechanical generalisation of thermodynamic entropy. We will now calculate its value.

7.2.2 Deriving statistical mechanical entropy

In order to fix the entropy difference between two states, it is necessary to find processes between the states in both directions, where:

$$\sum_m \frac{Q_m^{(1)}}{T_m^{(1)}} + \sum_n \frac{Q_n^{(2)}}{T_n^{(2)}} = 0 \quad (168)$$

For phenomenological thermodynamics, this involves reversible, quasistatic processes. These processes do not actually exist in reality. They are limiting processes - they are not necessarily attainable, but there is no physical reason one cannot get arbitrarily close to them. However, they are generally considered to only be possible for systems in thermal equilibrium.

In statistical mechanics we have a more general notion of process available: Hamiltonian dynamics. From this we can construct reversible processes¹³, as a limiting case.

1. Isothermal processes

We first identify the entropy change for an isothermal process. Taking an ideal heat bath as the limit of a real heat bath, we assume we can get arbitrarily close to an ideal heat bath process. An isothermal process in contact with a single heat bath at temperature T , requires mean work equal to:

$$\Delta \langle W \rangle = -kT \ln \left[\frac{Z(\tau)}{Z(0)} \right] \quad (169)$$

where

$$Z(t) = \text{Tr} \left[e^{-H(t)/kT} \right] \quad (170)$$

The mean change in energy is

$$\Delta E = \text{Tr} [H(\tau)] - \text{Tr} [H(0)] \quad (171)$$

The mean heat transferred to the heat bath is

$$\Delta Q = \Delta W - \Delta E \quad (172)$$

Substituting $E_n = -kT \ln Z - kT \ln [p_n]$ for canonical thermal systems gives

$$\Delta Q = kT \left(\sum_n p_n(\tau) \ln [p_n(\tau)] - \sum_n p_n(0) \ln [p_n(0)] \right) \quad (173)$$

¹³Please note, the specific Hamiltonians used are provided solely to demonstrate the existence of concrete examples.

2. Non-isothermal processes

While the above relationship may be well known for quasistatic, isothermal processes, we must consider a more general process. Suppose we have a system that starts in an arbitrary, uncorrelated state

$$\rho = \sum_n p_n |\alpha_n\rangle \langle \alpha_n| \quad (174)$$

with Hamiltonian H_i . We wish to find the entropy difference with another state

$$\rho' = \sum_n p'_n |\beta_n\rangle \langle \beta_n| \quad (175)$$

with Hamiltonian H_f . We need to find a reversible Hamiltonian process to achieve this.

We break the evolution into three stages, and give the Hamiltonian for each stage.

(a) $0 < t < \tau_1$

Keeping the system isolated

$$\begin{aligned} H_A = & H_i \left[\cos^2 \left(\frac{\pi t}{2\tau_1} \right) - \sin^2 \left(\frac{\pi t}{\tau_1} \right) \right] + H_1 \left[\sin^2 \left(\frac{\pi t}{2\tau_1} \right) - \sin^2 \left(\frac{\pi t}{\tau_1} \right) \right] \\ & - \frac{2i\hbar}{\tau_1} \sin^2 \left(\frac{\pi t}{\tau_1} \right) \ln \left[\sum_n |\gamma_n\rangle \langle \alpha_n| \right] \end{aligned} \quad (176)$$

with

$$H_1 = \sum_n -kT \ln(p_n) |\gamma_n\rangle \langle \gamma_n| \quad (177)$$

The effect of this evolution is to leave the system in the canonical state

$$\rho = \frac{e^{-H_1/kT}}{\text{Tr}[e^{-H_1/kT}]} = \sum_n p_n |\gamma_n\rangle \langle \gamma_n| \quad (178)$$

(b) $\tau_1 < t < \tau_2$

Bring the system into thermal contact with a heat bath at temperature T , and isothermally, quasi-statically change the Hamiltonian to

$$H_2 = \sum_n -kT \ln(p'_n) |\gamma_n\rangle \langle \gamma_n| \quad (179)$$

At the end of this process, the system is in the state

$$\rho = \frac{e^{-H_2/kT}}{\text{Tr}[e^{-H_2/kT}]} = \sum_n p'_n |\gamma_n\rangle \langle \gamma_n| \quad (180)$$

(c) $\tau_2 < t < \tau_f$

Isolate the system again and the final Hamiltonian is

$$\begin{aligned} H_B = & H_2 \left[\cos^2 \left(\frac{\pi t}{2(\tau_f - \tau_2)} \right) - \sin^2 \left(\frac{\pi t}{\tau_f - \tau_2} \right) \right] \\ & + H_f \left[\sin^2 \left(\frac{\pi t}{2(\tau_f - \tau_2)} \right) - \sin^2 \left(\frac{\pi t}{\tau_f - \tau_2} \right) \right] - \frac{2i\hbar}{\tau_f - \tau_2} \sin^2 \left(\frac{\pi t}{\tau_f - \tau_2} \right) \ln \left[\sum_n |\beta_n\rangle \langle \gamma_n| \right] \end{aligned} \quad (181)$$

which produces the desired final matrix ρ' .

Stages (a) and (c) are isolated, so involve no heat exchange. Changes in internal energy are entirely through work performed upon the system. In the limit of ideal heat baths and slow isothermal processes the net heat exchange is

$$\Delta Q = kT \left(\sum_n p'_n \ln [p'_n] - \sum_n p_n \ln [p_n] \right) \quad (182)$$

The limiting process can clearly take place in either direction. We can therefore deduce that, for any two density matrices ρ and ρ' , the difference in the statistical mechanical generalisation of their *thermodynamic* entropy is:

$$S [\rho'] - S [\rho] = -k \left(\sum_n p'_n \ln [p'_n] - \sum_n p_n \ln [p_n] \right) \quad (183)$$

As this relationship

$$S [\rho'] + k \sum_n p'_n \ln [p'_n] = S [\rho] + k \sum_n p_n \ln [p_n] \quad (184)$$

must hold for any density matrices, and with any eigenstates, then

$$S [\rho] = -k \text{Tr} [\rho \ln [\rho]] + c \quad (185)$$

where c is a universal additive constant which can be set to zero by convention. The Gibbs-von Neumann entropy is deduced to be the correct generalisation of the thermodynamic entropy, for statistical mechanics.

7.3 Optimal processes

The physical principle expressed by the Gibbs-von Neumann entropy is:

There is no process which takes a system from state A, to a system at state B, depositing mean heats Q_m into thermal systems at temperatures T_m , for which

$$S [B] - S [A] + \sum_m \frac{Q_m}{T_m} < 0 \quad (186)$$

The limiting process, where

$$S [A] = S [B] + \sum_m \frac{Q_m}{T_m} \quad (187)$$

is the *optimal* process. It is the process, which, on average, generates the least heat.

The thermal systems into which heat is transferred are not necessarily ideal heat baths. All that is assumed is that they are initially uncorrelated to other systems and that they are described by a canonical probability distribution.

There is no special reason why the *mean* generation of heat is important. Other criteria may be considered. In some physical circumstances other properties might be more important. One might wish to find the optimal process according to some other criteria, such as a minimax criteria (minimising the maximal cost). Statistical mechanics provides the tools for doing this.

If we search for a process which minimises the mean generation of heat in thermal systems, we are lead to the statistical mechanical entropy as the quantity which characterises the optimal process. If we search for a process by some other criteria, we will find different quantities of interest and different processes. These would, necessarily, involve at least as much heat generation, on average, but would outperform the optimal entropic process according to some other criteria.

7.4 Consistency

Can we be sure this definition of thermodynamic entropy is consistent? Once the identification of statistical temperature and the gas scale has been made, it is possible to derive the entropy relationships directly from the property of the Gibbs-von Neumann measure G , and the properties of canonical distributions. It holds for all processes, because of two properties of Hamiltonian evolutions:

1. For any process, which starts with uncorrelated distributions over a number of systems, the change in the value of G for each marginal distribution gives

$$\sum_i \Delta G_i \leq 0 \quad (188)$$

2. For any system, initially canonically distributed

$$\Delta G + \beta \Delta \langle H \rangle \geq 0 \quad (189)$$

We did not go directly from these properties to the identification of $-kG$ with the thermodynamic entropy as we wished to justify precisely what purpose thermodynamic entropy is intended to fulfil. Having done so, and demonstrated that $-kG$ is the correct value, we can now see that the result

$$\sum_i \Delta S_i \geq 0 \quad (190)$$

must hold, provided that the evolution is Hamiltonian and that initially independent systems are uncorrelated.

7.5 Non-equilibrium statistical mechanics

The entropy has been derived for arbitrary probability distributions, not only for systems in thermal equilibrium. Phenomenological thermodynamic entropy is frequently regarded as only being well defined for states in thermal equilibrium. How is it that statistical mechanics could do better?

There is a subtlety involved in the temperature in Equation 159. This gives the temperatures of the thermal systems, into which heat is transferred. It is not, directly, the temperature of the system from which heat is being expelled. It is the temperature of the heat baths, not the temperature of the system undergoing the cyclic process. The phenomenological thermodynamic entropy function, defined by Equation 161, is therefore defined for *all* states, whether they are in thermal equilibrium or not.

To identify the actual value of the entropy difference between two states, it is necessary to identify reversible processes in both directions. For phenomenological thermodynamics, such processes are only known in the limiting case of quasistatic processes on states in thermal equilibrium. Although the temperature T that appears in the summation is strictly the temperature of the *heat bath*, the change in S can usually only be uniquely identified when the system is kept in thermal equilibrium at the same T as the heat bath (see [Fer37][Chapter IV, Section 11]). This can lead to the claim that thermodynamic entropy is only well-defined for systems in thermal equilibrium.

While this may, arguably, be true for phenomenological thermodynamics, there is no reason to insist that it should also be true for statistical mechanics. Statistical mechanics comes with a well defined notion of processes - Hamiltonian evolution - even when systems are not in equilibrium. In statistical mechanics, there is no need to artificially restrict the domain of validity of the entropy function.

8 Conclusions

We have come to the conclusion that the Gibbs-von Neumann entropy is the appropriate statistical mechanical generalisation for thermodynamic entropy. This conclusion is reached based upon three considerations: that the dynamics of the system are Hamiltonian; that a probabilistic description is meaningful; and that thermal states are physically represented by canonical probability distributions.

No assumptions were required regarding whether thermal systems are subsystems of a large, microcanonically distributed system. Consequently, no assumptions regarding ergodicity or mixing are required. No assumptions regarding the size of the systems are involved, so no conclusions depend upon, or only hold true in, the thermodynamic limit. We have not assumed that the probability distribution only applies to microscopic degrees of freedom. Should probability distributions over macroscopically distinct states[Pen70] arise, the arguments still hold. Of particular importance, no restriction is made in its applicability to thermal systems or systems in equilibrium. The arguments that identify the Gibbs-von Neumann entropy for thermal systems, apply universally.

Beyond the use of a probabilistic description itself, no assumptions were made regarding entropy having a relationship to knowledge or information. It is quite unnecessary to consider information theory or properties of Shannon information. No relationship between thermal states and maximal ignorance need be assumed. Describing the Gibbs-von Neumann entropy as information theoretic seems unjustified, if not downright anachronistic¹⁴.

The physical understanding of the Gibbs-von Neumann entropy is shown to be precisely the generalisation one should expect, to statistical mechanics, of the thermodynamic entropy. The generalisation is from

There is no process which takes a system from state A, to a system at state B, depositing heats Q_m into thermal systems at temperatures T_m , for which

$$S[B] - S[A] + \sum_m \frac{Q_m}{T_m} < 0 \quad (191)$$

to

There is no process which takes a system from state A, to a system at state B, depositing *mean* heats Q_m into thermal systems at temperatures T_m , for which

$$S[B] - S[A] + \sum_m \frac{Q_m}{T_m} < 0 \quad (192)$$

The generalisation involved recognises that, with some probability, all of the classical statements of the second law of thermodynamics, are violated to any degree. The restriction expressed by the entropy function is not of the minimal heat generation for a Hamiltonian evolution of a given microstate, but of what is the minimum *expectation value* of the heat generated by Hamiltonian flows.

There remain many open questions in the understanding of statistical mechanics[Uff06]. We would like to develop how statistical mechanics may account for them, but this paper is far too long already. Of particular importance is the exploration of how the fine grained Gibbs-von Neumann

¹⁴The Gibbs entropy appears in 1902[Gib02] and the generalisation to quantum theory in 1932[Neu32]. The equivalent term does not appear in information theory until 1948[Sha48] and is not generalised to quantum theory until 1994[JS94].

entropy accounts for the appearance of irreversibility and time-asymmetry. On the question of whether this entropy is subjective, and ‘observers’ may affect the entropy of a system, in the manner of a Maxwellian Demon, see[Mar02]. There are many other measures, microscopic and macroscopic, of probability distributions and of individual states, that are presented as ‘entropies’. While they may have useful roles to play, the question is: are they the statistical mechanical generalisation of *thermodynamic* entropy?

Once the canonical distribution is accepted as appropriate for thermal states, the Gibbs-von Neumann entropy follows inevitably for all probability distributions, microscopic or macroscopic. In Section 5 it is shown that the canonical distribution can be uniquely identified, solely from considering the observed properties of thermal states themselves. The relationship:

$$\sum_i \frac{\Delta Q_i}{T_i} \geq 0 \quad (193)$$

for closed cycles, is then a derived property of Hamiltonian dynamics and serves to *define* the statistical mechanical generalisation of entropy, in the same way that the Clausius relationship defines phenomenological entropy. To quote a recent paper¹⁵:

The rule ... that associates heat transfer with entropy holds only for thermodynamic entropy and, indeed, defines it. No other entropy can satisfy it without at once also being thermodynamic entropy.[Nor05]

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¹⁵The views of which are, nevertheless, quite different to the views of this paper!

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